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# THE IDENTITY OF PENROSEITE AND BLOCKITE

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Penroseite (Gordon, 1926) was the first native nickel selenide to be discovered; and until so-called blockite was described (Herzenberg and Ahlfeld, 1935) penroseite also possessed the distinction of carrying more selenium than any other known mineral. Gordon found that penroseite possesses three perfect cleavages mutually at right angles and a fourth distinct prismatic cleavage (110) for which he gave no angular measurements. He concluded that the mineral possesses orthorhombic symmetry, but it is obvious that he might equally well have considered the symmetry to be tetragonal or cubic. Herzenberg and Ahlfeld gave no crystallographic data for blockite but found from chemical analysis that the mineral is accurately represented by a formula of the type $RSe_2$, the predominant metals being nickel and copper. They based their distinction of blockite from penroseite on the much higher lead content of the latter (17.13% for penroseite, 0.35% for blockite) and on the higher selenium content of blockite. Cubic nickel diselenide possessing the pyrite type of crystal structure has been prepared by de Jong and Willems (1928).

It is obviously desirable to study further the relationship between penroseite and blockite, and at the same time to determine whether the symmetry and crystal structure of the two minerals is identical with that of artificial nickel diselenide. The supposed difference in composition of penroseite and blockite also calls for new chemical analyses accompanied by *x*-ray and specific gravity data. For this study the following specimens from the mineral collections of the British Museum (Natural History) were available:

(1) Penroseite: a massive lead-grey fragment ($3\frac{1}{2}\times3\times1$ cm.) showing bladed cleavages, labelled Colquechaca, Bolivia (broken from type specimen). Cavities in this specimen are lined with pseudomorphs of limonite after chalybite, and a portion of the surface is stained green due to nickel and carries a thin brick-red incrustation, presumably of "ahlfeldite" [B.M. 1926, 1].

(2) Blockite: a nodule 3 cm. diameter, compact massive in the centre, shelly-concentric towards the exterior; coated with limonite. Locality, Hiaco mine, 30 Km. E.N.E. of Colquechaca, dep. Potosi, Bolivia [B.M. 1936, 126].

(3) Blockite: a compact matrix of chalybite and quartzite (8×6×3 cm.) enclosing lead-grey nodules up to 2 cm. across showing radiating curved segments and "ahlfeldite." Locality, Hiaco mine, Colquechaca, dep. Potosi, Bolivia [B.M. 1935, 1186].

*X*-ray photographs of small cubic cleavage fragments detached from specimens 1, 2 and 3 were taken and proved to be identical in pattern and intensity, conforming to cubic symmetry and revealing the pyrite type of crystal structure (figs. 1, 2). Small but appreciable differences in unit-cell size were, however, discovered. With a view primarily to assist the chemical analyses, small quantities of each specimen were also examined with a quartz spectrograph using the electric arc. No difference in the lead content could be detected, but the lines due to silver increase in intensity in the order A, B, C (fig. 3). In order to test the sensitivity of the lead lines comparison photographs, under the same conditions, were also made of mixtures of powdered arc carbon and litharge containing 1% and 10% lead. These preliminary results show quite definitely that penroseite and blockite have the same symmetry and crystal structure and that, whilst the lead content is almost constant, there is some

Table 1. Chemical Analyses of Penroseite.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Se | 67.01 | 66.59 | 67.31 | 59.80 | 69.72 | 72.90 |
| S | 0.39 | 0.52 | tr. | — | — | — |
| Ni | 8.89 | 9.88 | 10.30 | 11.14 | 14.09 | 27.10 |
| Co | 1.10 | 0.71 | 0.52 | 1.34 | 2.45 | — |
| Fe | tr. | 0.72 | 0.72 | 1.08[1] | 1.29 | — |
| Cu | 4.50 | 3.72 | 3.55 | 7.84 | 6.70 | — |
| Hg | 1.45 | 4.12 | 1.41 | — | 1.95 | — |
| Pb | 13.72 | 10.88 | 8.27 | 17.13 | 0.35 | — |
| Ag | 2.13 | 5.00 | 7.78 | 2.04 | 1.73 | — |
| Pt metals | — | — | — | — | 0.022 | — |
| Insol. | — | — | — | — | 1.28 | — |
| | 99.19 | 102.14 | 99.86 | 100.37 | 99.58 | 100.00 |
| Unit cell edge | 6.017 | 6.001 | 6.001 | — | — | 6.022 Å |
| Sp. Gr.[2] $D^{18^\circ}_{4^\circ}$ | 6.87 | 6.71 | 7.0 | 6.93 | 6.05 | 6.69[3] |

1. Penroseite [B.M. 1926, 1]. Microanalysis by M. H. H.
2. Blockite [B.M. 1936, 126]. Microanalysis by M. H. H.
3. Blockite [B.M. 1935, 1186]. Microanalysis by M. H. H.
4. Penroseite, Bolivia; analyst Whitfield (Gordon, 1926).
5. Blockite, Bolivia; analyst Herzenberg (Herzenberg and Ahlfeld, 1935).
6. $NiSe_2$.

[1] $Fe_2O_3$.

[2] Determined on portions of about 10 mg. by a micromethod shortly to be described.

[3] Specific gravity calculated from the *X*-ray data and the ideal composition $NiSe_2$ is 6.54.

variation in silver content. Microchemical analyses (table 1) confirm these conclusions.

*Chemical Methods.* Owing to the rather short time at our disposal it was not possible to make a really adequate study of the possible methods for the microanalysis of penroseite; the methods adopted are thus not ideal, but since partial repeats by other methods have given good agreement it is felt that the analyses are reasonably accurate.

The method adopted was to dissolve the mineral (20 mg.) in hydrochloric acid (1:1) with small additions of potassium chlorate in the cold; solution took about three days.[4] The residue of silver chloride and insoluble matter was filtered off, dried, and weighed, then the silver chloride dissolved out with sodium thiosulphate and the residue of insolubles weighed. In the filtrate excess chlorine was destroyed by the dropwise addition of concentrated solution of hydrazine hydrochloride, then selenium precipitated by the addition of a solution of hydrazine hydrochloride in hydrochloric acid (1:1) saturated with sulphur dioxide. After standing over night the precipitate was filtered off, washed, dried and weighed. Subsequent examination showed that in addition to selenium it contained the whole of the mercury as calomel.

The filtrate from this precipitate was evaporated to dryness, the hydrazine present being destroyed by occasional additions of nitric acid. The residue was dissolved in a little water, 0.1 cc. of strong sulphuric acid added to the mixture, evaporated in the water bath, diluted and filtered ($PbSO_4$). The filtrate from the lead sulphate was precipitated with salicylaldoxime in acetic acid solution and the precipitate filtered off, dried, and weighed. This proved to be an unfortunate step as contrary to the experience of Ephraim (1928) a large proportion of the nickel was carried down (no detailed study of this separation was made, and it is possible that under suitable conditions it might prove to be an efficient one). It was therefore, necessary to re-dissolve this precipitate in hot hydrochloric acid, and precipitate the nickel with dimethylglyoxime in ammoniacal solution; after filtering off and weighing this (a part of the nickel present) the copper was precipitated with pyridine and thiocyanate. In the filtrate from the salicylaldoxime precipitate the remaining nickel was precipitated with dimethylglyoxime, then the iron with cupferron and the cobalt with $\alpha$-nitroso-$\beta$-naphthol. Mercury was determined in a separate portion by a titration with diphenylthiocarbazone according to the method of Fischer and Leopoldi (1935). The aqueous layer after this titration was used for the determination of sulphur as $BaSO_4$.

TABLE 2. ATOMIC RATIOS OF PENROSEITE ON THE BASIS OF $(R, Ag_2)=1$
(Numbers refer to Table 1)

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Se | 2.617 | 2.425 | 2.539 | 1.175 | 2.055 |
| S | 0.038 | 0.047 | — | — | — |
| Ni | 0.467 | 0.484 | 0.523 | 0.430 | 0.559 |
| Co | 0.058 | 0.035 | 0.026 | 0.052 | 0.097 |
| Fe | — | 0.036 | 0.038 | 0.031 | 0.054 |
| Cu | 0.218 | 0.168 | 0.166 | 0.279 | 0.245 |
| Hg | 0.022 | 0.059 | 0.021 | — | 0.023 |
| Pb | 0.204 | 0.151 | 0.119 | 0.187 | 0.004 |
| Ag | 0.061 | 0.133 | 0.215 | 0.043 | 0.037 |

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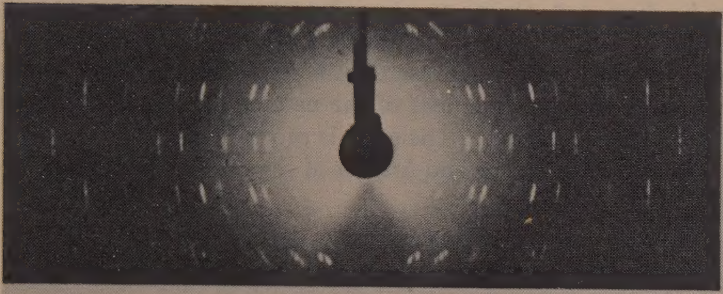
[4] Solution in bromine water was rather quicker, but left some doubts as to the state of combination of the mercury in the selenium—calomel precipitate.

As was to be expected in view of the heterogeneous nature of the material, the atomic ratios yield little information except that the new analyses show selenium very markedly in excess of the formula (R, $Ag_2$)$Se_2$.

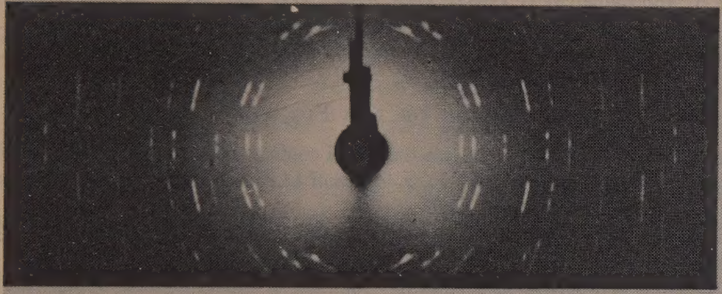
The question immediately arises: are specimens of penroseite and blockite intergrown with small variable amounts of other minerals similar in appearance but different in chemical composition? There are two distinct methods available for testing this possibility: The optical examination of polished sections and *x*-ray examination.

*Optical Examination.* Gordon states that polished sections of penroseite show thin veins of silver selenide but no optical study of blockite has yet been published. The minerals most likely to be intergrown with penroseite and blockite are cubic in symmetry, such as clausthalite, PbSe, naumannite (Ag, Pb)Se, and argentiferous galena (Pb, Ag)S. The sulphur content as shown by chemical analysis is so small that the galena content must be less than 3% .We should expect polished sections of all these to be optically isotropic, hence differentiation is only possible if we can detect differences of colour and reflectivity. A further restriction to optical methods is inherent in the formation of penroseite and blockite. The innermost portion of the nodules is compact, massive and lacks the cleavage boundaries which are so conspicuous nearer the surface. An examination of polished sections of penroseite and blockite nos. 1 and 2 both showed clearly thin veins of a pale mineral which Gordon thought to be silver selenide. The veins of no. 1 are numerous but very thin whereas in no. 2 the veins attain a width of ½ mm. in one or two places. They are most readily seen by oblique illumination under a binocular microscope when their tin-white colour contrasts well with the darker slightly yellowish grey of the penroseite or blockite. Using a vertical illuminator and polarised light it was found that both minerals are isotropic; no third metallic component could be detected.

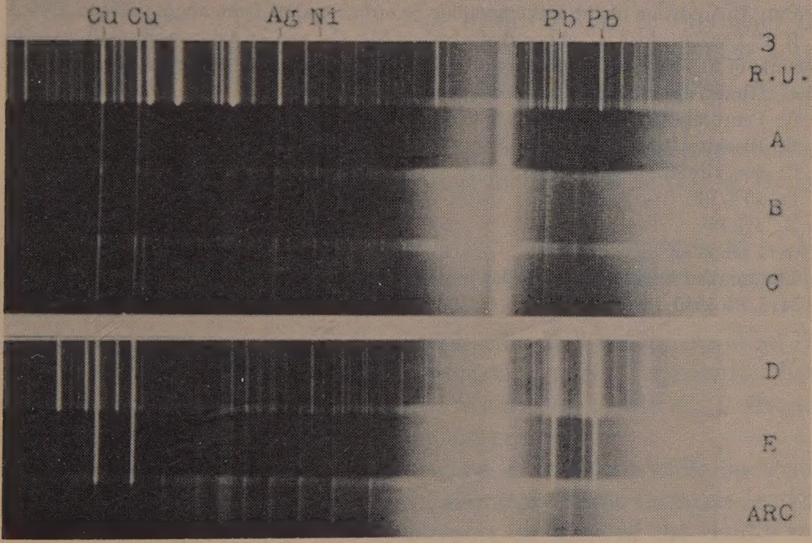
*X-ray examination.* A fine steel needle was used to excavate some of the white mineral discovered in the polished sections of 1 and 2. A stationary *x*-ray photograph of the fragments obtained proves to be a powder photograph of a mineral with cubic symmetry and face-centred lattice with *a* 6.12 Å. On the same photograph flecks due to a little adherent penroseite yield unit cell dimensions 6.00 Å. The photograph except for the flecks due to penroseite is identical with one of naumannite from Tilkerode, Harz [B.M. 95201]. Hence it is now certain that both the specimens of penroseite and blockite are intergrown with naumannite and that the variation in silver and lead content is at least partly due to admixture with that mineral. Analyses 1, 2 and 3 suggest, however that penroseite contains both combined lead and silver. Penroseite and



1



2



3

blockite may therefore be regarded as identical minerals and the latter name may be discarded. Owing to varying proportions of naumannite, specimens yield chemical analyses varying in lead and silver content; and the true composition of penroseite still remains uncertain. It has already been noted that a fragment of the naumannite gives a powder not a single crystal photograph. Thence it is probable that the naumannite is an infilling of the cracks and fissures of the more coarsely crystalline penroseite.

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Herzenberg, R., and Ahlfeld, F. (1935): *Cbl. Min.*, A, 189, 277—*Min. Abs.*, **6**, 147.

## EXPLANATION OF THE FIGURES

The *x*-ray photographs were taken with unfiltered copper radiation, $\lambda = 1.539$ Å, and with a cylindrical camera, diameter 6.04 cm. A length of 11.85 cm. on the original films is equivalent to 10 cm. on the reproduced figures.

Fig. 1. Rotation photograph of a cleavage of fragment of penroseite [B.M. 1926, 1] about the axis [100].

Fig. 2. Rotation photograph of a cleavage fragment of blockite [B.M. 1935, 1186] about this axis [100].

Fig. 3. A portion of the spectrographic record extending from about 3200 to 3700 Å.

R. U. Powder which is composed of a base of Mg, Ca, and Zn oxides and small, varying amounts of 51 elements in such proportions that only a few of the most sensitive lines (raies ultimes) appear in the emission spectra.

A. Penroseite [B.M. 1926, 1].
B. Blockite [B.M. 1936, 126].
C. Blockite [B.M. 1935, 1186].
D. 10% Pb.
E. 1% Pb.
Arc. Carbon arc alone.

The marked lines have the following wave-lengths: Cu 3247 Å, Cu 3274, Ag 3383, Ni 3415, Pb 3640, Pb 3683.

# CRYSTALLOGRAPHIC STUDIES IN THE VIVIANITE GROUP

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## Contents

Acknowledgment . . . . . 325
Measurements with the Two-Circle Goniometer . . . . . 326
  Erythrite . . . . . 326
  Cabrerite . . . . . 328
  Annabergite and Köttigite . . . . . 328
*X*-ray measurements . . . . . 329
  Vivianite . . . . . 329
  Erythrite . . . . . 331
  Cabrerite . . . . . 332
  Bobierrite . . . . . 333
Unit Cell and Crystallographic Orientation . . . . . 334
Space Group Determination . . . . . 336
Optical Studies . . . . . 336
Summary . . . . . 340
References . . . . . 341

## Acknowledgment

By courtesy of Professor Charles Palache the present writer, when still a regular staff member of the Geophysical Laboratory, was enabled to spend about five weeks of the summer of 1935 in the laboratories of the Mineralogical Museum at Harvard University. The chief object was to study a rock series from Iceland and the Faeroe Islands; but a visit to Harvard, this centre of crystallographic research, afforded also unique opportunities for studies in classical crystallography. When the writer expressed a desire to do some research work in this field, Dr. Palache kindly suggested a re-study of erythrite; he supplied the necessary material from the collections of the Museum, and himself selected some of the best crystals for goniometer measurements.

Dr. M. A. Peacock kindly offered to teach the writer the new methods and schemes of presentation worked out for the new edition of Dana's Mineralogy.

For the hospitality and the stimulating influence he received at the Mineralogical Museum the writer wishes to express his sincere appreciation.

All *x*-ray work was done at the Geophysical Laboratory. As usual Dr. W. F. Foshag kindly supplied the necessary mineral specimens from the U.S. National Museum. Thanks are also due to Mr. C. J. Ksanda for having taken many of the *x*-ray photographs.

The experimental part of the present paper was done while the writer was connected with the Geophysical Laboratory of the Carnegie Institution of Washington. A preliminary report on some of the results was given at the Sixteenth Annual Meeting of the Mineralogical Society (1935); but owing to various circumstances the writing of the final paper has been delayed for one year.

## MEASUREMENTS WITH THE TWO-CIRCLE GONIOMETER

*Erythrite*, Cobalt bloom, $Co_3As_2O_8 \cdot 8H_2O$. The crystals are prismatic, show few faces, and are always striated vertically, usually also parallel to [101]. For these reasons few good goniometer measurements exist and the crystallographic constants are not known with any great accuracy. The results of measurements by Des Cloizeaux (1908) and Green (1910) are given below. Later studies by Lincio (1914) and Shannon (1926) did not lead to new values for the geometrical elements.

New measurements were carried out on erythrite crystals supplied by Prof. Palache from the Karabacek Collection in the Mineralogical Museum of Harvard University. Table 1 gives the crystal elements derived from the best measurements and the mean measured and calculated angles for the accepted forms. The orientation of V. Goldschmidt for vivianite has been retained.

TABLE 1. ERYTHRITE FROM SCHNEEBERG, SAXONY; TWO-CIRCLE MEASUREMENTS ON EIGHT CRYSTALS

Monoclinic; $a:b:c=0.7648:1:0.7122$; $\beta=105°02'$
$p_0:q_0:r_0=0.9312:0.6878:1$; $\mu=74°58'$
$p_0'=0.9642$, $q_0'=0.7122$, $x_0'=0.2686$

| Forms | No. of Faces | Measured | | | | Calculated | |
|---|---|---|---|---|---|---|---|
| | | Range | | Mean | | $\phi$ | $\rho$ |
| | | $\phi$ | $\rho$ | $\phi$ | $\rho$ | | |
| c 001 | — | — | — | — | — | 90°00′ | 1 |
| b 010 | 16 | −2°40′ to 3°30′ | — | 0°27′ | 90°00′ | 0 00 | 9 |
| a 100 | | Vertical zone very poor. No faces could be determined uniquely, but there are broad chains of reflections very roughly corresponding to the positions of 100, 110 and 610 | | | | 90 00 | 90 00 |
| m 110 | | | | | | 53 33 | 90 00 |
| n 610 | | | | | | 82 59 | 90 00 |
| w $\bar{1}01$ | 6* | −85 48 to 93 02 | 34°50′ | −89 40 | 34 50 | −90 00 | 34 49½ |
| p 111 | 6 | 61 16 to 59 50 | 54 16 to 55°10′ | 59 50 | 54 57½ | 59 59 | 54 55 |
| v $\bar{1}11$ | 5 | −44 17 to −44 25 | 44 48 to 44 58 | −44 21 | 44 53 | −44 19½ | 44 52½ |
| q $\bar{6}16$ | 2† | −80 16 to −82 21 | 35 03 to 35 11 | −81 18 | 35 01 | −80 19 | 35 12½ |
| n 101 | 1 | — | — | 89 41 | 51 07 | 90 00 | 50 57 |

* Vicinals.

† Vicinals to ($\bar{1}01$), indications of faces were seen throughout the zone from ($\bar{1}01$) to ($\bar{6}16$).

These figures and their relative accuracy will be discussed in a later section after the presentation of the x-ray studies.

Fig. 1*a* depicts the typical crystal habit, the large *b*-face is characteristic, the relative size of the upper terminal faces is however subject to some variations, but very regularly the same combination of faces is

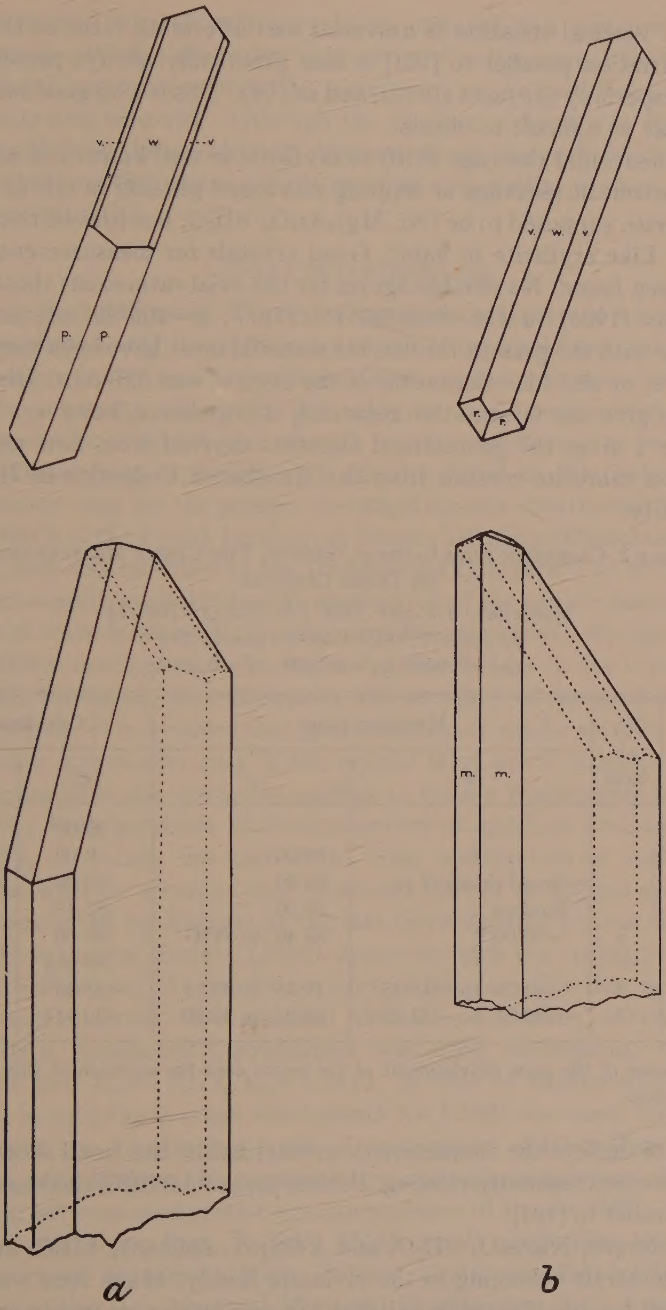

FIG. 1. (a) Erythrite from Schneeberg, Saxony. (b) "Cabrerite" (=annabergite) from Laurion, Greece.

present. Vertical striation is universal and affects all faces of the zone [001]; striation parallel to [101] is also practically always present and affects especially the faces *b*(010), and *w*($\bar{1}01$). This is why good measurements are so difficult to obtain.

The pinacoidal cleavage (010) in erythrite is well known; in addition to it a prismatic cleavage or slipping was found parallel to *r*($\bar{1}12$).

*Cabrerite*, supposed to be $(Ni, Mg)_3As_2O_8 \cdot 8H_2O$, but proved to contain no Mg. Like erythrite in habit. Good crystals for measurements have never been found. No reliable figures for the axial ratio exist; those given by Sachs (1906): $a:b:c=0.82386:1:0.77677$; $\beta=106°29'$ are at great variance with the present results; his material must have been very poor, therefore, or else his orientation of the crystal was different. His paper does not give any information regarding this question, however.

Table 2 gives the geometrical elements derived from new measurements on cabrerite crystals from the Karabacek Collection in Harvard University.

TABLE 2. CABRERITE FROM LAURION, GREECE; TWO-CIRCLE MEASUREMENTS ON THREE CRYSTALS

Monoclinic: $a:b:c=0.7874:1:0.7223$; $\beta=104°31\tfrac{1}{2}'$
$p_0:q_0:r_0=0.9195:0.6993:1$; $\mu=75°28\tfrac{1}{2}'$
$p_0'=0.9498$; $q_0'=0.7224$; $x_0'=0.2591$

| Forms | No. of faces | Measured range | | Calculated | |
|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | $\phi$ | $\rho$ |
| *c* 001 | — | — | — | 90°00′ | 14°31½′ |
| *b* 010 | | — | 90°00′ | 0 00 | 90 00 |
| *a* 100 | | Broad chains of reflections | 90 00 | 90 00 | 90 00 |
| *m* 110 | | | 90 00 | 52 45 | 90 00 |
| *w* $\bar{1}01$ | 3 | −90°00′* | 34 40 to 34°47′ | 90 00 | 34 38 |
| *p* 111 | — | — | — | 59 08½ | 54 37½ |
| *v* $\bar{1}11$ | 3 | −42 24 to −43°55′ | 44 35 to 46 15 | −43 43 | 44 59 |
| *r* $\bar{1}12$ | 5 | −30 11 to −32 18 | 22 04 to 22 20 | −30 51½ | 22 49 |

* Because of the poor development of the prism zone the azimuth of this face was taken as zero.

Fig. 1*b* depicts the characteristic crystal habit; the small faces *r*($\bar{1}12$) are, however frequently missing. Perfect pinacoidal (010) cleavage. Striation parallel to [101].

*Annabergite*, $Ni_3As_2O_8 \cdot 8H_2O$, and *Köttigite*, $Zn_3As_2O_8 \cdot 8H_2O$, are additional minerals belonging to the vivianite family. Much time was spent in search for small crystals suitable for goniometer measurements, but without much success. With the kind assistance of Dr. Harry Berman of the Mineralogical Museum at Harvard we finally succeeded in getting a few faceted crystals which could be oriented and measured on the goniometer. Within the rather large error of measurement the observed interfacial angles were found to correspond to the analogous angles of erythrite and cabrerite. Although the number of faces was insufficient for establishing the geometrical elements, it can be concluded from these measurements that the constants must be very similar to those of erythrite and cabrerite.

## *X*-RAY MEASUREMENTS

By optical goniometry the crystallographic constants of a mineral can be established only if a sufficient number of external faces is developed; if there are few or poorly developed faces, no values or uncertain values for the constants will result. By using an *x*-ray goniometer accurate values can be obtained even though no external faces may be present. The Weissenberg arrangement is ideally suited to this purpose. The instrument used for the present investigation was constructed by Brækken (1932) of the Fysisk Institutt of Norges Tekniske Höiskole at Trondheim, and was modified at the Geophysical Laboratory so as to render it more readily available for the application of the equi-inclination technique in accordance with the scheme of Buerger (1934). By this method the lattice spacings and the angles between planes in the crystal were directly measured. As will be seen, the accuracy of the method is very satisfactory. It is believed that greater accuracy can be secured with the reflection goniometer only if the crystal faces are of a high degree of excellence. It is also obviously possible to build a Weissenberg apparatus for very high precision of determination of spacings and angles and thereby, of course, the axial ratio. The construction of such an apparatus with an accuracy said to exceed that of an optical goniometer was announced by Buerger at the last (seventeenth) annual meeting of the Mineralogical Society (1936). But even with the ordinary Weissenberg arrangement the results are very satisfactory. By this method the following minerals were studied: vivianite, erythrite, cabrerite, and bobierrite. Unfiltered Cu-radiation was used throughout, the wave lengths are: $\lambda_{\alpha_1}=1.5373$, $\lambda_{\alpha_2}=1.5410$; in case of superposition of the $\alpha_1$ and $\alpha_2$ spot the average wave length $\lambda=1.5388$ was used. Other symbols used are: $\theta$=glancing angle, $\mu'$=separation of layer lines; $a_0$, $b_0$,$c_0$ are the periods along the corresponding crystallographic axes; $d_{hkl}$ is the spacing between consecutive structure planes of the set (*hkl*).

*Vivianite*, monoclinic, $Fe_3P_2O_8\cdot 8H_2O$. Small needle-like, transparent crystals from Monserrat Mine, Bolivia, kindly supplied by Dr. W. F. Foshag of the U.S. National Museum, Washington, D.C., were used in the present röntgenographic investigation. The habit of the crystals permitted an easy orientation of the *c*-axis, and they were therefore mounted on the Weissenberg goniometer for rotation around this axis. Ordinary rotation, equator, and layer-line photographs were obtained. The diffraction spots were measured and indexed, and the lattice spacings determined in the usual way, see table 3. Particularly useful for an exact determination of the crystallographic angle $\beta$ are diffraction spots from faces of the form ($h0l$), and the glancing angles of these faces are most accurately determined from the rotation diagrams around the $c$-axis.

TABLE 3. VIVIANITE FROM MONSERRAT, BOLIVIA; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$a_0=10.039$, $b_0=13.388$, $2c_0=9.374$; $\beta=104°18'$

| Indices | $\theta°$ | $b_0$ |
|---|---|---|
| 0 2 0 | 6.61 | 13.368 |
| 0 4 0 | 13.29 | 13.388 |
| 0 8 0 | 27.37 | 13.388 |
| 0 10 0 | 35.04 | 13.388 |
| 0 12 0 | 43.57 | 13.386 |
| 0 16 0 | 66.72 | 13.389 |
| Average | | 13.388 |

| Indices | $\theta°$ | $d_{100}$ |
|---|---|---|
| 2 0 0 | 9.32 | 9.723 |
| 4 0 0 | 18.44 | 9.730 |
| 6 0 0 | 28.33 | 9.728 |
| 8 0 0 | 39.21 | 9.727 |
| 10 0 0 | 52.20 | 9.728 |
| 12 0 0 | 71.48 | 9.728 |
| Average | | 9.728 |

| | $\mu'°$ | $c_0$ |
|---|---|---|
| 1st layer | 19.17 | 4.687 |
| 2nd layer | 41.05 | 4.687 |
| Average | | 4.687 |

| Indices | $\theta°$ | $(\beta-90)°$ |
|---|---|---|
| 0 0 1 | 9.765 | 14°23′ |
| $\bar{2}$ 0 1 | 11.61 | 14 18 |
| 2 0 1 | 15.00 | 14 17 |
| Average | | 14 18 |

The table shows that the $c$-dimension of the structural lattice is halved as compared with the morphological lattice. Consequently:

$$a:b:c=\frac{a_0}{b_0}:\frac{b_0}{b_0}:\frac{2c_0}{b_0}=0.7499:1:0.7002$$

$$\beta=104°18'; \text{ density}=2.711.$$

The probable error of the axial ratio can be estimated by inspection of table 3. A further check on these figures is supplied by a recent paper by Yamaguti (1936) which became available to me after the present manuscript was written. By the cathode ray diffraction method he determined the crystallographic constants of vivianite as follows:

$$a_0=9.997\ \text{Å},\ b_0=13.37\ \text{Å},\ c_0=4.696\ \text{Å};\ \beta=104°16'.$$

Vivianite is not a rare mineral and is frequently encountered in well

TABLE 4. LINEAR GEOMETRICAL ELEMENTS OF VIVIANITE

| $a:b:c$ | $\beta$ | Author |
|---|---|---|
| 0.7488:1:0.7029 | 104°33′ | Cesàro |
| 0.7498:1:0.7017 | 104 26 | Goldschmidt |
| 0.7499:1:0.7002 | 104 18 | $x$-ray (Barth) |

developed faceted crystals which at various times have been measured with the reflection goniometer. As seen from table 4 the results obtained from the present $x$-ray study agree closely with the crystallographic elements of vivianite as determined on the reflection goniometer by earlier workers, e.g., Cesàro (1897), Goldschmidt (1913).

Personally the writer believes that the geometrical elements of a crystal can be more accurately determined with the present $x$-ray goniometer than is usually possible with a reflection goniometer. This is, of course, especially true for crystals with few or poorly developed faces. Several members of the vivianite group are encountered in such imperfect crystals that no determination of the crystallographic constants have been attempted. For other members the constants were known only approximately. In such cases the $x$-ray method is indispensable.

*Erythrite*, $Co_3As_2O_8 \cdot 8H_2O$. Thin crystal fragments flattened after (010)

TABLE 5. ERYTHRITE FROM SCHNEEBERG, SAXONY; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$a_0 = 10.184$, $b_0 = 13.340$, $2c_0 = 9.460$; $\beta = 105°01'$

| Indices | $\theta^\circ$ | $b_0$ |
|---|---|---|
| 0 8 0 | 27.48 | 13.331 |
| 0 10 0 | 35.18 | 13.343 |
| 0 12 0 | 43.79 | 13.325 |
| 0 14 0 | 53.77 | 13.340 |
| 0 16 0 | 67.03 | 13.356 |
| Average | | 13.340 |

| Indices | $\theta^\circ$ | $d_{100}$ |
|---|---|---|
| 4 0 0 | 18.23 | 9.838 |
| 8 0 0 | 28.00 | 9.832 |
| 10 0 0 | 51.38 | 9.839 |
| Average | | 9.836 |

| | $\mu^\circ$ | $c_0$ |
|---|---|---|
| 1st layer | 18.99 | 4.729 |
| 2nd layer | 40.58 | 4.730 |
| Average | | 4.730 |

| Indices | $\theta^\circ$ | $(\beta-90)^\circ$ |
|---|---|---|
| $\bar{2}$ 0 1 | 11.40 | 15°11′ |
| $\bar{4}$ 0 1 | 18.36 | 14 51 |
| 2 0 1 | 14.94 | 15 00 |
| 6 0 1 | 32.58 | 15 05 |
| 8 0 1 | 43.55 | 14 59 |
| Average | | 15 01 |

were used. They were mounted on the Weissenberg goniometer and $x$-ray pictures were obtained in the same way as for vivianite. The most important measurements are given in table 5.

The $x$-ray data lead to the following constants:

$$a:b:c=\frac{a_0}{b_0}:\frac{b_0}{b_0}:\frac{2c^0}{b_0}=0.7633:1:0.7092;\beta=105°01'$$

Density = 3.182[1]

Since crystals of erythrite are never well suited for measurements with the reflection goniometer it is probable that the most accurate values for the crystallographic elements are those obtained from the present $x$-ray measurements; the probable limit of error can be estimated by inspection of table 5. Table 6 gives a comparison of all available independent determinations of the geometrical elements of erythrite.

TABLE 6.—LINEAR CRYSTALLOGRAPHIC ELEMENTS OF ERYTHRITE

| $a$ | $b$ | $c$ | $\beta$ | Author |
|---|---|---|---|---|
| 0.7937 | 1 | 0.7356 | 105°09′ | Des Cloizeaux |
| 0.7502 | 1 | 0.7006 | 105 01 | Green |
| 0.7648 | 1 | 0.7122 | 105 02 | Barth (optical) |
| 0.7633 | 1 | 0.7092 | 105 01 | Barth ($x$-ray) |

*Cabrerite*, $Ni_3As_2O_8 \cdot 8H_2O$ (proved to be annabergite). Only thin and flaky crystals were available; they are always very flexible and proved to be more or less bent and distorted and gave relatively poor $x$-ray photographs. The results are therefore not as accurate as those for vivianite or erythrite. It was possible in this case to mount a flaky little crystal on the Weissenberg goniometer for rotation around the $b$-axis. The crystallographic angle $\beta$ could thus be measured directly and graphically on the film. Various spacings necessary for computation of the crystallographic elements were determined from additional Weissenberg photographs as shown in table 7.

Consequently:

$$a:b:c=\frac{a_0}{b_0}:\frac{b_0}{b_0}:\frac{2c_0}{b_0}=0.7619:1:0.7073;\ \beta=104°45'.$$

Although these figures are not very accurate they probably represent the most accurate values of the geometrical elements of cabrerite thus far available. They probably are superior to those deduced from reflection goniometer measurements.

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[1] Previous density determinations are: 2.912 Kersten (1893); 2.948 Dana (1892); 3.178 de Schulten (1903).

Table 7. Cabrerite from Laurion, Greece; Measurement of Lattice Spacings of the Most Important Planes

$a_0=10.122$, $b_0=13.284$, $2c_0=9.396$; $\beta=104°45'$

| Indices | $\theta°$ | $d_{100}$ |
|---|---|---|
| 2 0 0 | 8.99 | 9.847 |
| 4 0 0 | 18.38 | 9.760 |
| 6 0 0 | 28.14 | 9.802 |
| 10 0 0 | 51.86 | 9.773 |
| 12 0 0 | 70.28 | 9.799 |
| Average | | 9.7835 |

| Indices | $\theta°$ | $2d_{001}$ |
|---|---|---|
| 0 0 1 | 9.64 | 9.189 |
| 0 0 2 | 19.84 | 9.068 |
| 0 0 3 | 30.51 | 9.093 |
| 0 0 5 | 57.80 | 9.084 |
| Average | | 9.0815 |

| | $\mu'°$ | $b_0$ |
|---|---|---|
| 1st layer | 6.60 | 13.387 |
| 2nd layer | 13.40 | 13.280 |
| 3rd layer | 20.37 | 13.262 |
| 4th layer | 27.60 | 13.286 |
| 5th layer | 35.40 | 13.281 |
| 6th layer | 44.07 | 13.277 |
| 7th layer | 54.15 | 13.289 |
| 8th layer | 67.90 | 13.287 |
| Average | | 13.284 |

*Bobierrite*, $Mg_3P_2O_8 \cdot 8H_2O$. Occurs in aggregates of minute, white, needle-like crystals. Much time was spent in search of a crystal suited for measurements with the reflection goniometer, but in vain. Nor are any older measurements on record. In order to determine the crystallographic constants of this mineral we have therefore in this case the choice between the *x*-ray method and no method at all. Material for the present study was supplied from both Harvard University (Dr. Palache) and U. S. National Museum (Dr. Foshag). The needle-like crystals permit orientation on the Weissenberg goniometer only of one zone, the *c*-axis. Without changing the orientation of the crystal a set of Weissenberg photographs was produced from which all the crystallographic constants were determined as shown in table 8.

This table demonstrates an interesting fact: the doubling of the *b*-axis as compared with vivianite, erythrite, and cabrerite. Thus we obtain:

$$a:b:c=\frac{a_0}{\frac{1}{2}b_0}:\frac{\frac{1}{2}b_0}{\frac{1}{2}b_0}:\frac{2c_0}{\frac{1}{2}b_0}=0.7193:1:0.6671;\ \beta=104°01',$$

as the geometrical elements of bobierrite. The density is 2.169. These

TABLE 8. BOBIERRITE FROM MEXILLONES, CHILE; MEASUREMENT OF LATTICE SPACINGS OF THE MOST IMPORTANT PLANES

$a_0=9.946$, $\frac{1}{2}b_0=13.827$, $2c_0=9.279$; $\beta=104°01'$

| Indices | $\theta$ | $b_0$ |
|---|---|---|
| 0 4 0 | 6.42 | 27.656 |
| 0 8 0 | 12.86 | 27.654 |
| 0 16 0 | 26.44 | 27.646 |
| 0 20 0 | 33.81 | 27.654 |
| Average | | 27.654 |

| Indices | $\theta$ | $d_{100}$ |
|---|---|---|
| 2 0 0 | 9.12 | 9.7082 |
| 4 0 0 | 18.62 | 9.6387 |
| 6 0 0 | 28.55 | 9.6587 |
| 8 0 0 | 39.62 | 9.6520 |
| 10 0 0 | 52.83 | 9.6470 |
| Average | | 9.650 |

| | $\mu'°$ | $c_0$ |
|---|---|---|
| 1st layer | 19.37 | 4.640 |
| 2nd layer | 41.56 | 4.639 |
| Average | | 4.6395 |

| Indices | $\theta°$ | $(\beta-90)°$ |
|---|---|---|
| 2 0 1 | 15.06 | 13.75 |
| $\bar{2}$ 0 1 | 11.72 | 14.28 |
| Average | | 14.02 |

values are, however, susceptible of improvement. All crystals studied proved to be more or less distorted and composed of several fibres of slightly different orientation. Furthermore, all reflections from planes of the form $(h0l)$, which are particularly useful for the determination of the angle $\beta$, are either absent or very weak. The rotation photographs could not be used, therefore, for this determination; instead the zone curves were sketched on the first layer-line photographs, and the position of the wanted reflections thus fixed. But, of course, this procedure cannot give results as accurate as those for vivianite or erythrite.

## UNIT CELL AND CRYSTALLOGRAPHIC ORIENTATION

In his *Atlas der Krystallformen* V. Goldschmidt has set the standard crystallographic orientation of the minerals of the vivianite family. In the present $x$-ray study the unit cell has been chosen so as to correspond to the orientation of Goldschmidt. It is not possible, however, to bring the unit cell demensions into exact agreement with the axial ratio of Goldschmidt. In vivianite, erythrite, and cabrerite the $c$-axis of the structural lattice is halved as compared with the morphological lattice, otherwise there is exact correspondence. However, the unit cell so far considered is not the "true" unit cell. As mentioned before it was thus chosen in order to make the results of the $x$-ray analyses directly comparable with those of the reflection goniometer. The interrelation of the three cells thus far mentioned: (1) the morphological cell, (2) the unit cell used in the present study, and (3) the true unit cell, is brought out by fig. 2.

The question has recently been discussed by several American crystallographers whether the geometrical elements of a compound determined with the reflection goniometer should necessarily be exactly the same as those obtained from the unit cell dimensions established by $x$-ray analyses (Donnay, Tunell & Barth 1934). In 1933 George Tunell and the present writer expressed the belief that it is not desirable to stretch the results of the two methods of inquiry—with the reflection goniometer and the $x$-ray goniometer—into exact correspondence, although there should be a simple relation between them in all cases, and an exact correspondence in many.

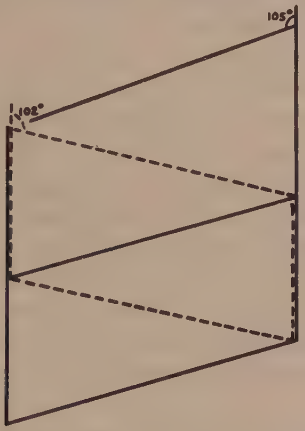

Fig. 2. Projection on (010) showing the mutual relationship of the three different cells mentioned in the text. The morphological cell is not a structural unit, it is represented by the full drawing, angle $\beta$ is about 105°. The unit cell used in the present investigation is half the morphological cell and has the same orientation and the same angle $\beta$ as the morphological cell; it is shown by full lines. The true unit cell is shown by stippled lines; the orientation is different from that of the morphological cell, angle $\beta$ is about 102°, its volume is half that of the morphological cell.

If the morphological description of crystals of the vivianite type could be simplified by use of the true unit cell, a re-orientation of vivianite would seem desirable. However, no such advantage exists. The transformation: morphological cell $(hkl)\rightarrow$true unit cell, $(h'k'l')$ is:

$$h' = -(h+\tfrac{1}{2}l);\ k' = k;\ l' = \tfrac{1}{2}l.$$

If this transformation is tried, e.g., for erythrite or vivianite (all known faces are given by V. Goldschmidt) it is seen that no simplification of the indices results. Thus the present mineral group seems to constitute a case where the crystal morphology should not be described in terms of the true unit cell.

In bobierrite the true unit cell is similar to that of the other minerals except that the *b*-axis is doubled. But since very few crystal faces have been observed in bobierrite it is impossible to tell which lattice would best suit the morphology. It seems natural, however, to use the same morphological lattice for bobierrite as for the other members of this mineral family.

## SPACE GROUP DETERMINATION

Crystallographic measurements on vivianite, erythrite, and "cabrerite," indicate that these minerals belong to the holohedral class of the monoclinic syngony. The *x*-ray diffraction spots indicate a base-centerde underlying lattice, consequently $C_{2h}^6$ and $C_{2h}^3$ are possible space groups. But $C_{2h}^6$ is excluded by the fact that diffraction spots from faces of the form $(00l)$ with $l$ odd and $(h0l)$ with $h$ even and $l$ odd are present in the diagrams. All space group criteria are however in agreement with $C_{2h}^3$, which is therefore regarded as the correct space group of these minerals.

Bobierrite is not isomorphous with the same space group (as indicated e.g., by the presence of diffraction spots from faces of the form $(0kl)$ with both $k$ and $l$ odd). The ordinary space group criteria lead to $C_{2h}^5$, but in addition to the extinctions demanded by this space group, there are a few additional systematic extinctions probably due to the doubling of the *b*-axis.

No endeavour was made to elucidate the atomic arrangement of any of these minerals.

## OPTICAL STUDIES

Natural minerals as well as artificial products were examined. The following compounds were synthesized: $Ni_3As_2O_8 \cdot 8H_2O$ (annabergite), $Mg_3As_2O_8 \cdot 8H_2O$ (hörnesite), and $Mg_3P_2O_8 \cdot 8H_2O$ (bobierrite). The procedure of de Schulten (1903) was followed. The synthetic crystals were too small, however, for measurements with the goniometer, but their optical constants could be determined with the microscope. A survey of the optical properties of the minerals of the vivianite group has been given by Larsen (1921), by Ulrich (1926), and by Larsen and Berman (1934). For comparison some of their data are included in table 9.

Several interesting points are brought out by this table: First we shall consider the data for bobierrite. In this mineral as well as in artificial $Mg_3P_2O_8 \cdot 8H_2O$ the crystallographic *b*-axis coincides with the direction of the optical normal. This is contrary to the data given by Lacroix (1888), by Ulrich, and by Larsen and Berman who state that the plane of the optical axes is normal to (010).[2] But new, careful comparative

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[2] In the first issue of Larsen (1921) the optical orientation of bobierrite is given as: $Y=\beta$, which is in agreement with the new measurements by the present writer. The different statement in the second edition is therefore probably a misprint.

Table 9. Optical Properties of Some Minerals of the Vivianite Group

| Mineral | $\alpha$ | $\beta$ | $\gamma$ | $c:\gamma$ | Orient. | Author |
|---|---|---|---|---|---|---|
| Cabrerite | 1.62 | 1.654 | 1.689 | 33° | $b=\alpha$ | Larsen |
| Cabrerite | — | 1.650 | 1.688 | 36 | $b=\alpha$ | Barth |
| Annabergite | 1.622 | 1.658 | 1.687 | 36 | $b=\alpha$ | Larsen |
| Annabergite | — | 1.651 | 1.689 | 30 | $b=\alpha$ | Barth |
| $Ni_3As_2O_8 \cdot 8H_2O$ | — | 1.655 | 1.688 | 32 | $b=\alpha$ | Barth |
| Hörnesite | 1.563 | 1.571 | 1.596 | 31 | $b=\alpha$ | Larsen |
| $Mg_3As_2O_8 \cdot 8H_2O$ | — | 1.570 | 1.594 | 45 | $b=\alpha$ | Barth |
| Bobierrite | 1.510 | 1.520 | 1.543 | 29 | $b=\beta$* | Larsen |
| Bobierrite | 1.510 | — | 1.543 | 30 | $b=\beta$ | Barth |
| $Mg_3P_2O_8 \cdot 8H_2O$ | 1.510 | — | 1.543 | 30 | $b=\beta$ | Barth |
| $Mg_3P_2O_8 \cdot 8H_2O$ | — | — | — | — | $b=\alpha$ | Ulrich |

* Larsen and Berman (1934) give $b=\alpha$.

studies of bobierrite, vivianite, annabergite, etc. proved beyond doubt that the *b*-axis coincides with the direction of index $\beta$ in all bobierrite material used in the present investigation, both natural and synthetic. In this respect bobierrite differs from all other minerals of the vivianite group (fig. 3). The fact that the spacing of the *b*-axis is doubled in bobierrite, as compared with the other minerals of this group, may have something to do with the difference in optical behaviour.

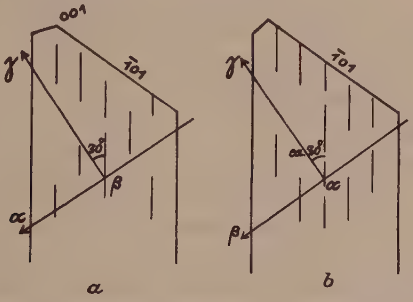

Fig. 3. (a) Optical orientation of bobierrite. (b) Optical orientation of all other minerals of the vivianite group.

In this connection mention should be made of an old paper by Michel (1893) who introduces the name *hautefeuillite* for a bobierrite-like mineral which, according to his analysis, differs from bobierrite in that it contains 5.71% CaO, and in its optical orientation. However, the redetermined optical properties of bobierrite correspond to those of hautefeuillite as given by Michel, viz.: "Le plan des axes optiques est compris dans $g^1$ (010)", and "L'indice moyen $n_m = 1.52$ (raie D)" (1893, p. 39). It may be reasonable to suppose, therefore, that Michel's hautefeuillite is not a new mineral, but ordinary bobierrite. The presence of CaO in the analysis is easily explained by contamination of apatite with which it is associated in nodular intergrowths. Michel's chief argument for establishing a new mineral species was the fact that the optical orientation of his mineral differed from that of bobierrite as given by Lacroix. But the results of the present study indicate that Lacroix was wrong in his optical determination, and that Michel thus was the first to establish the correct optical orientation of bobierrite. However, it is not impossible that bobierrite can take up a certain amount of CaO, although an isomorphous replacement of Mg by Ca is rather unlikely from a crystallochemical point of view. Nor is the existence of lime-bearing bobierrites sustained by the present study. Until more convincing evidence is produced, therefore, it seems best to discard hautefeuillite as a mineral name.

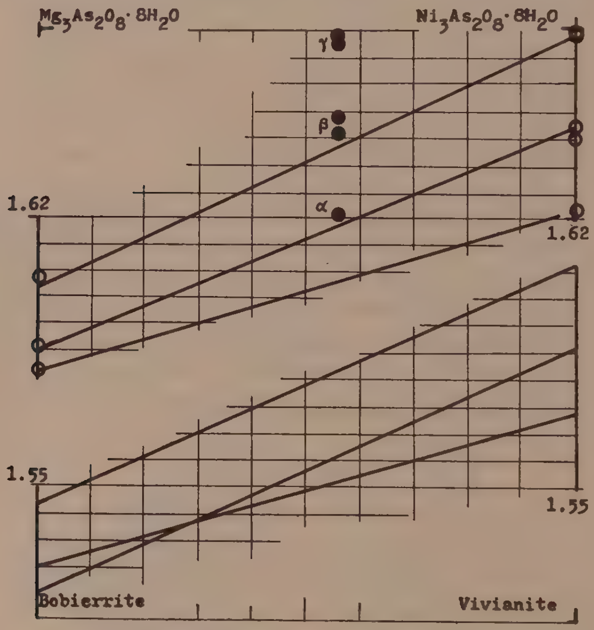

FIG. 4. Refractive indices of mixed crystals of the system $Mg_3As_2O_8\cdot 8H_2O-Ni_3As_2O_8\cdot 8H_2O$. ○=Hörnesite. ○=Annabergite ●=Cabrerite from Laurion. The alleged composition of cabrerite from Sierra Cabrera is approximately the same as that of cabrerite from Laurion.

It might be added that surprisingly little is known about the formation of mixed crystals in the vivianite family. For crystallochemical reasons one would, for instance, expect bobierrite to take up FeO (not CaO) with formation of mixed crystals towards the composition of vivianite. It is much more probable that such crystals exist than that hautefeuillite exists. It is worth noticing that owing to the different optical orientation of the two end components certain members of the iron-bearing bobierrite series in all probability would be optically uniaxial (fig. 4).

Another interesting point brought out by table 9 is the position of cabrerite in the binary system $Ni_3As_2O_8 \cdot 8H_2O$—$Mg_3As_2O_8 \cdot 8H_2O$. In fig. 4 a graphical survey is given of the optical properties of minerals and artificial compounds belonging to the system. The minerals annabergite and hörnesite are supposed to represent essentially the Ni-bearing and the Mg-bearing end-member respectively, and their optical properties are in complete agreement with this. Cabrerite is supposed to be a mixed crystal between these end-members,[3] but its optical properties are in direct conflict with this assumption. To be sure, the optical properties of so-called cabrerite are practically identical with those of annabergite and of pure $Ni_3As_2O_8 \cdot 8H_2O$. We can conclude, therefore, that cabrerite from Laurion which has been studied both by Larsen and by the present author, is essentially pure $Ni_3As_2O_8 \cdot 8H_2O$, i.e. annabergite, in spite of the analyses by Damour and by Sachs; for even a small amount of MgO would have evinced its presence in this mineral by decreasing the refractive indices. In this type of mixed crystals with very close crystallographic relationship between the two end-members (for the crystallography of hörnesite see Zambonini, 1919) the values of the refractive indices are directly proportional to the change in the composition (Barth, 1930).

The only other known occurrence of so-called cabrerite is Sierra Cabrera in Spain. The establishment of the mineral species rests on two very old analyses, one by Ferber (1863), and one by Frenzel (1874), which may or may not be trustworthy. Ferber's analysis shows 9.29% MgO, that of Frenzel 6.94% MgO—a rather large difference on presumably the same material—the corresponding contents of $Mg_3As_2O_8 \cdot 8H_2O$ in the mix-crystal is 46 and 34 mol. per cent respectively. The refractive indices of a mixed crystal of about this composition is shown by fig. 4. Unfortunately no optical data on cabrerite from Sierra Cabrera are on record, nor has material been available for new studies. It is highly desirable that an optical analysis of this material be carried out. If the values of the refractive indices should support the assumption of a magnesia-rich mixed crystal (cabrerite) this would be the first example of a mineral series of mixed crystals with extensive replacement of Ni by Mg. However, before such data are available it seems best to discard cabrerite as a mineral name.

De Schulten (1903) claimed to have made synthetic cabrerite by dropping into a dilute solution of $HNa_2As_4 \cdot 7H_2O$ first magnesium sulphate, whereby hörnesite forms, then a mixture of magnesium sulphate and nickel sulphate whereby the hörnesite crystals are said to grow bigger and turn green—thereby becoming cabrerite. There is hardly any doubt, however, that this procedure would lead to the formation of zoned crystals, the total composition of which, as determined by de Schulten, has no direct relation to the actual composition of the various solid phases.

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[3] Analyses by Des Cloizeaux and Damour (1878) and by Sachs (1906) on cabrerite from Laurion show 4.64 and 9.34% MgO respectively.

## SUMMARY

The geometrical elements of a crystal can be more accurately determined with an $x$-ray goniometer than is usually possible with a reflection goniometer. This is, of course, especially true for crystals with few or poorly developed faces. Several members of the vivianite group are encountered in such imperfect crystals that no determination of the crystallographic constants had been attempted. For other members the constants were known only approximately.

New $x$-ray measurements as well as reflection goniometer measurements on this series of minerals have been carried out, and the crystallographic constants of the several members have been established (table 10).

TABLE 10. LINEAR GEOMETRICAL ELEMENTS OF THE MINERALS OF THE VIVIANITE GROUP

| Mineral | Composition | $a$ | $b$ | $c$ | $\beta$ | Method |
|---|---|---|---|---|---|---|
| Vivianite | $Fe_3P_2O_8 \cdot 8H_2O$ | 0.7499 | 1 | 0.7002 | 104°18′ | $x$-ray[1] |
| Symplesite | $Fe_3As_2O_8 \cdot 8H_2O$ | 0.7806 | 1 | 0.6812 | 107 17 | reflect. gon.[2] |
| Bobierrite | $Mg_3P_2O_8 \cdot 8H_2O$ | 0.7193 | 1 | 0.6671 | 104 01 | $x$-ray[1] |
| Hörnesite | $Mg_3As_2O_8 \cdot 8H_2O$ | 0.7676 | 1 | 0.7182 | 104 25 | reflect. gon.[3] |
| Erythrite | $Co_3As_2O_8 \cdot 8H_2O$ | 0.7634 | 1 | 0.7092 | 105 01 | $x$-ray[1] |
| Erythrite | $Co_3As_2O_8 \cdot 8H_2O$ | 0.7648 | 1 | 0.7122 | 105 02 | reflect. gon.[1] |
| Annabergite | $Ni_3As_2O_8 \cdot 8H_2O$ | 0.7619 | 1 | 0.7073 | 104 45 | $x$-ray[1] |
| Annabergite | $Ni_3As_2O_8 \cdot 8H_2O$ | 0.7874 | 1 | 0.7223 | 104 31½ | reflect. gon.[1] |
| Köttigite | $Zn_3As_2O_8 \cdot 8H_2O$ | 0.7 | 1 | 0.7 | 105 | |

[1] New data.

[2] Krenner (1886).

[3] Zambonini (1919).

The unit cell used in this $x$-ray study was chosen so as to have the same crystallographic orientation as the morphological cell. The absolute dimensions of this cell are given in table 11. But it should be borne in mind that this cell is not the same as the so-called true unit cell (fig. 2).

A survey of the optical properties of minerals and artificial products belonging to the vivianite group is given in table 9. The mineral names

TABLE 11. ABSOLUTE DIMENSIONS OF THE UNIT CELL OF VIVIANITE, BOBIERRITE, ERYTHRITE, AND ANNABERGITE

| Mineral | $a_0$ | $b_0$ | $c_0$ | $\beta$ | Density |
|---|---|---|---|---|---|
| Vivianite | 10.039 | 13.388 | 4.687 | 104°18′ | 2.711 |
| Bobierrite | 9.946 | 27.654 | 4.6395 | 104 01 | 2.169 |
| Erythrite | 10.184 | 13.340 | 4.730 | 105 01 | 3.182 |
| Annabergite | 10.122 | 13.284 | 4.698 | 104 45 | 3.231 |

hautefeuillite and cabrerite have been discarded. They were supposed to stand for Ca-bearing bobierrite and Ni-bearing annabergite, respectively. But it has been demonstrated that in their optical properties, as far as the determinations go, they do not differ from those of the end-members; and that thus far no compelling evidence has been produced proving the existence of any such mixed crystals either in Nature or among artificial products.

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# CONSTITUTION AND CLASSIFICATION OF THE NATURAL SILICATES

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## Contents

I. General Introduction and Theory .... 342

- Introduction .... 342
- Older Concepts Concerning the Constitution of the Silicates .... 343
- Results of the *X*-ray Analyses of Silicate Structures .... 345
- A Theory of the Constitution of the Silicates, Derived from *X*-ray Structural Studies; and Some Relevant Definitions .... 348
- A Classification Based on the Theory .... 351

II. A Tabulated Arrangement of the Silicates According to the New Classification .... 355

III. Discussion of the Classification .... 365

- Silica Type .... 365
- Disilicate Type .... 375
- Metasilicate Type .... 386
- Pyrosilicate Type .... 393
- Orthosilicate Type .... 395

References .... 402

Index of species .... 405

## I. GENERAL INTRODUCTION AND THEORY

### Introduction

The silicic acid theory of the constitution of the silicates and the classification based on that theory is almost as old as the science of Mineralogy (Doelter 1914). Except for the important modifications by Tschermak, of which more will be said in the next section, the theory is essentially today as it was in 1811, and the classification now used in most textbooks is the same as that found in texts more than fifty years old. One may assume, then, that no adequate substitute for this firmly established classification has as yet been presented. Within the past ten years, however, a re-examination of the constitution of the silicates has become possible through *x*-ray structural studies due mainly to the Braggs.

As a result of this new method of attack a new conception of silicate structure has been evolved and a classification which logically follows from that conception has been proposed by Bragg (1930), Machatschki (1928), and others. Most of the suggestions for a new classification have remained only suggestions. Many papers have appeared in the past ten years in which the new silicate theories have been used to study particular minerals or mineral groups. Winchell has classified the silicates which have thus far been studied structurally. No one, within the writer's knowledge, has made a systematic investigation of all the well-defined silicates, in order to ascertain the extent to which the newer theories are valid, and how well a classification based on these theories meets the requirements of descriptive mineralogy. It is the purpose of this paper to present the evidence for the validity of the newer concepts and to give a more complete classification based on them.

The writer wishes to acknowledge the interest and encouragement shown by Professors Palache and Larsen of the Department of Mineralogy at Harvard University, as well as their advice in the preparation of this paper. To Professor B. E. Warren of the Massachusetts Institute of Technology the writer expresses his thanks for having introduced him to the interesting *x*-ray data available on this subject. Professor W. E. Ford of Yale University and Professor A. L. Parsons of the University of Toronto have read the manuscript and have offered valuable criticism. Dr. M. A. Peacock has suggested improvements in the form of the manuscript.

## Older Concepts Concerning the Constitution of the Silicates

Doelter (1914) gives a comprehensive summary of the various theories on the constitution of the silicates. For this reason a full discussion need not be given here. It is worthy of note, however, that Tschermak made his first contribution to the study of the chemistry of the feldspars in 1864, and that his paper gave for the first time a real picture of isomorphism in the silicates. It is well also to remember that Tschermak (1864) anticipated the requirement of similar atomic constitution in isomorphous compounds. He wrote the formulae for the plagioclases (p. 37):

| | |
|---|---|
| Anorthite | $Ca_2Al_2Al_2Si_4O_{16}$ |
| Albite | $Na_2Al_2Si_2Si_4O_{16}$ |

and today, with our more precise knowledge of the structure of the feldspars, we find that his formulae stand as written. So also he showed the true nature of the chemical relationships in the scapolites and the chlorites, to name a few of the important groups examined by him. Tschermak examined the facts closely and with great skill. He interpreted his findings in a way that is unacceptable in the light of the newer theories derived from *x*-ray studies; but to him must go the honor of being the greatest worker in the field of mineral chemistry.

Clarke (1914) brought to a culmination the studies of a century in this field. He listed (p. 14) the silicic acids necessary to explain the constitution of the silicates. To these he attributed acid, basic and normal salts forming silicate compounds. He wrote elaborate structural formulae, extreme examples of which appear on pages 68 and 69 of his book.

The real difficulties in the older interpretations arose from the fact that no direct evidence was available upon which to construct an adequate theory. Most of the earlier workers, including Tschermak, attempted first of all to synthesize the various hypothetical silicic acids which they postulated as the basis of the silicate compounds found in nature. Failing in this, they attempted to identify the acids in solutions of the minerals themselves; but this method likewise brought no success. Clarke, searching for some other method of attack, studied the alteration products of the silicates, and thus deduced a relation between their formulae, as he expressed them. The writer believes that this method was no more successful than the others, and for the same reasons.

There have been attempts to study the silicates by analogy with organic compounds (Asch 1914). These have not proved fruitful and are rightly discarded. Short-lived theories which fell of their own weight, so to speak, have been proposed from time to time; an account of these may be found in Doelter (1914).

The problem of the constitution of the silicates is a problem in crystal chemistry, because the silicates are with but few exceptions solid crystalline compounds as we know them in nature. To bring a silicate into solution necessarily destroys the arrangement we are trying to study. To alter the substance by solution, or in any other way, likewise destroys its former constitution. These methods are not adequate for the problem at hand and they fail, therefore, to yield the true answer.

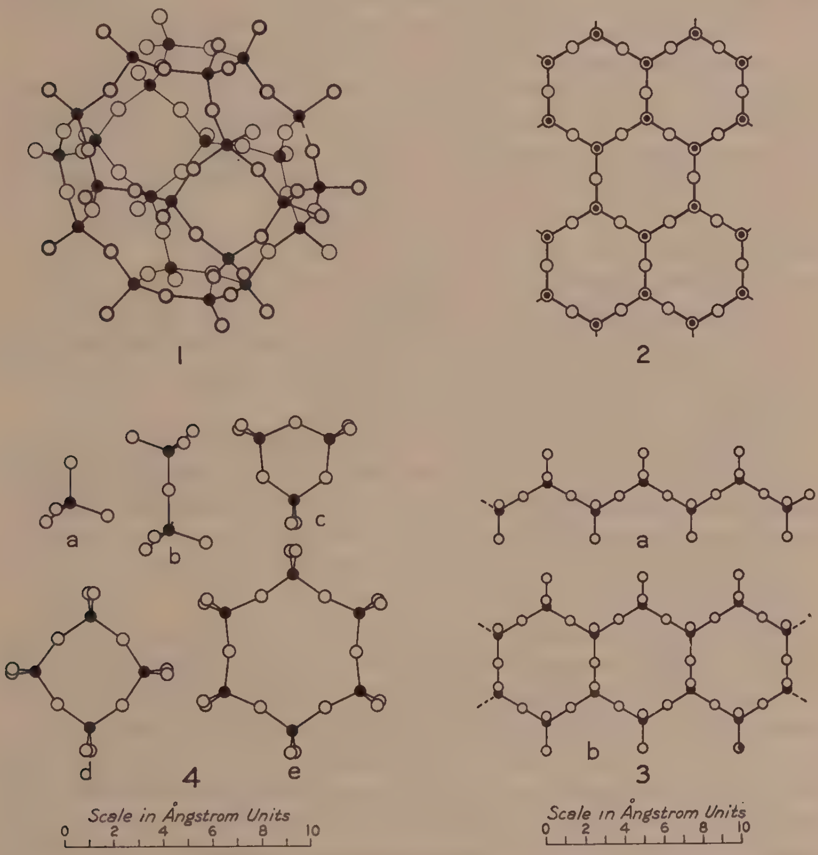
The *x*-ray method, by which the substance is studied as it is, as a crystal, can hope to solve the problem of its constitution; and this method has already proved fruitful. The recognition of the peculiar ability of this new tool to solve problems in crystal chemistry has led to an enormous amount of experimental work in the new field. The silicates have been particularly studied by Bragg (1930) and his students. Thus far the crystal structures of some forty silicates have been definitely established. Among these are some of the commonest minerals. The structures of many more silicates are incompletely known. Those silicates for which structures have been determined amount to perhaps ten or fifteen per cent of all the species listed in Dana's textbook (1932).

Since the underlying principles of the structures in silicates were soon recognized by workers in this field, the structures already determined represent the main types. It is because of this that a general examination as proposed in this paper can be undertaken with some hope of success, despite the comparatively small number of specific structures determined.

## RESULTS OF THE *X*-RAY ANALYSES OF SILICATE STRUCTURES

The material of this section is taken largely from the summary of the knowledge of silicate structures, by Bragg (1930). Here only the data immediately useful to our purpose are given.

In order of importance the general features revealed by the *x*-ray studies, are given below.



Linkages of silicon-oxygen tetrahedra. Black, silicon, with or without aluminum; white, oxygen. After Bragg (1930).

FIG. 1. Silica type, $SiO_2$; three-dimensional linkage.

FIG. 2. Disilicate type, $Si_2O_5$; two-dimensional linkage.

FIG. 3. Metasilicate type; a. $SiO_3$, single-chain linkage; b. $Si_4O_{11}$, double-chain linkage.

FIG. 4. a. Orthosilicate type, $SiO_4$; independent tetrahedra. b. Pyrosilicate type, $Si_2O_7$; paired tetrahedra. c. Ring-linkage, $Si_3O_9$. d. Ring-linkage, $Si_4O_{12}$. e. Ring-linkage, $Si_6O_{18}$.

1. In all silicates examined the silicon-oxygen relation is found to be the same; a silicon atom always occurs in the center of four oxygen atoms arranged as a tetrahedron about it. This tetrahedron is the fundamental and apparently invariable unit in the silicate structure (Fig. 4a).

2. The different silicate types arise from the various ways in which the silicon-oxygen tetrahedra in a given structure are related to each other. The rule that tetrahedra can share corners only, and not sides or edges, has been found to be universally true; consequently two tetrahedra can have only one oxygen in common between them. However, every oxygen of every tetrahedron may be shared with another tetrahedron.

3. There are characteristic ways in which tetrahedra have been found to combine in the silicates examined, and these ways of linkage are comparatively few in number. If the tetrahedra are not combined with each other, the composition of the silicate is of the $SiO_4$ type; if all the corners are shared with other tetrahedra, the composition is that of the different forms of silica, $SiO_2$. Other relations yield intermediate types. The list is given below.

A. Three dimensional networks (Silica type): All the tetrahedra share their corners with other tetrahedra giving a three dimensional network. Silica, in any of its modifications, is the type substance of this linkage, which results in the composition $SiO_2$ (Fig. 1).

B. The sheet structure (Disilicate type): This structure is obtained when tetrahedra are placed all in one plane with each tetrahedron being joined to other tetrahedra by three atoms lying in the common plane. An indefinite extension of this linkage produces a hexagonal network in the plane. The type silicate of this structure is mica, with the composition $Si_2O_5$ (Fig. 2).

C (1). Chain structures (Metasilicate type): Tetrahedra joined together, to produce chains of indefinite extent. There are several modifications of this structure yielding somewhat different compositions: (a) A single chain; one long linkage of tetrahedra of indefinite extent producing a composition $SiO_3$, as in the pyroxenes (Fig. 3a). (b) A double chain, giving a composition $Si_4O_{11}$, as in the amphiboles (Fig. 3b). (c) A sort of triple chain, with some modifications (Ito 1933), yielding $Si_3O_8$ compositions. Other methods of linking tetrahedra in chains to form $Si_3O_8$ compositions have not yet been thoroughly investigated.

(2) Ring structures (Metasilicate type): Two of the tetrahedral corners shared, as in the chains, but instead of extending indefinitely in one direction the chains make closed units of a ring-like structure. Benitoite with the $Si_3O_9$ ring (Fig. 4c), and beryl with the $Si_6O_{18}$ ring (Fig. 4e) are type examples.

D. Double tetrahedra structures (Pyrosilicate type): These structures arise from two tetrahedra with a common oxygen between them. The resulting composition is $Si_2O_7$ (Fig. 4b), and the type mineral is thortvietite.

E. Independent tetrahedral groups (Orthosilicate type): In this type none of the tetrahedra shares corners with another. The resultant composition is $SiO_4$ (Fig. 4a) and the type mineral is olivine.

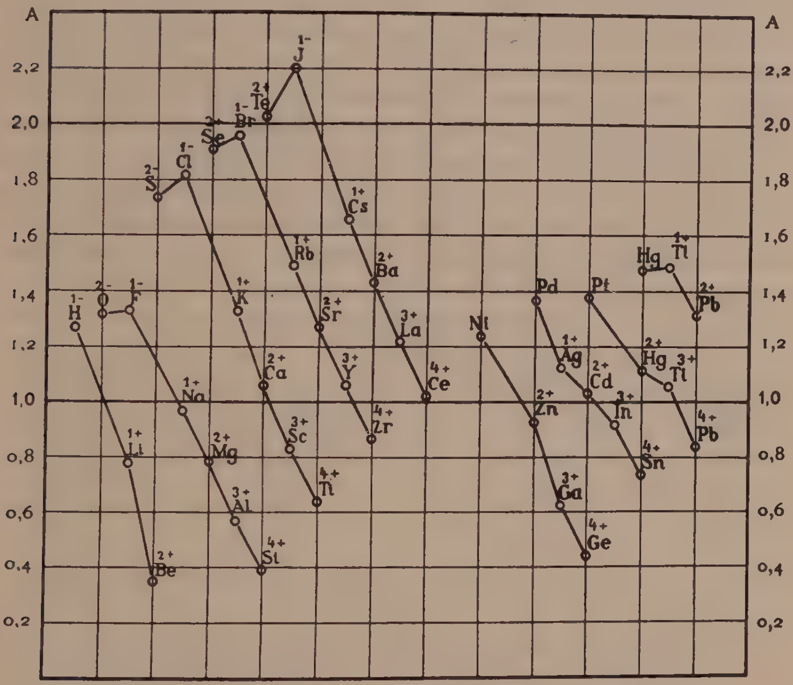


FIG. 5. Ionic radii of some elements including those commonly found in the silicates. After Goldschmidt (1926).

4. Since the oxygen atoms are usually the largest in the structure as found by measurement of ionic radii (Goldschmidt 1926), these atoms are chiefly responsible for the size of the unit cell. From this it follows that the number of oxygen atoms in the formula of a silicate is highly significant.

5. Silicates which are members of an ismorphous series (see later section) have formulae with the same number of oxygens (Berman 1929).

6. It is inferred from $x$-ray studies that the general type of substitution in isomorphous silicates is atom for atom, regardless of valence, and

that the chief factor governing such substitution is similarity of the volumes of the atoms concerned (Zambonini 1922, Wherry 1923, Goldschmidt 1926). This leads to the conclusion that the total number of atoms in isomorphous minerals is the same. There are some exceptions to this rule, which will be noted as they occur in the classification (Warren 1930 A; Berman and Larsen 1931).

7. *X*-ray studies have definitely led to the concept of the substitution of Al for Si in a large number of silicates, where the Al occurs in tetrahedra similar to the tetrahedra about the Si (Warren 1930).

8. It has been noted (Bragg 1930) that the elements found in the silicates, as well as in many other compounds, usually have a characteristic arrangement of oxygen about them, regardless of the compound. The number of oxygens characteristically associated with an atom is known as its *co-ordination number*. Some atoms have two or three co-ordination numbers. Below is a list of the elements commonly found in the silicates and their co-ordination numbers, as observed in determined structures.

TABLE 1. CO-ORDINATION NUMBERS
(BRAGG 1930)

| Element | Co-ordination numbers | Element | Co-ordination numbers |
|---|---|---|---|
| Be | 4 | Ti | 6 |
| B | 3, 4 | Mn″ | 4, 6, 8 |
| Na | 6, 8 | Fe″ | 4, 6, 8 |
| Mg | 4, 6, 8 | Fe‴ | 4?, 6 |
| Al | 4, 5, 6 | Zn | 4 |
| Si | 4 | Zr | 8 |
| Ca | 6, 7, 8 | Ba | 6, 12 |
| Sc | 6 | | |

## A THEORY OF THE CONSTITUTION OF THE SILICATES, DERIVED FROM *X*-RAY STRUCTURAL STUDIES; AND SOME RELEVANT DEFINITIONS

If we accept the accumulated evidence of the structural studies of the silicates, we must conclude that the old silicic acid theory is untenable. In its place we must postulate that the chief variations in the constitution of silicates are due to the various ways, already mentioned, in which the fundamental motif, namely the silicon-oxygen tetrahedron, combines with its neighboring tetrahedra to form more or less complex groups extending indefinitely throughout the crystal. This concept, and the various types of silicates arising from it, is not just another way of indicating a new group of silicic acids, because the silicates cannot be regarded, in this new theory, as acid radicals with the metallic elements. We must think of the silicates as frameworks of silicon-oxygen tetrahedra indefinitely extended in the crystal. Typical acid compounds are made up of discrete radicals not joined together like the silicate tetrahedra.

Corresponding to different linkages of the tetrahedra we have different compositions, habits and physical properties in the several types of silicates. The sheet structure, for instance, produces the platy form of the micas, the chlorites, the kaolins and other minerals, as discussed later. The chain structures produce prismatic or fibrous crystals as exemplified in the pyroxenes and amphiboles. The three-dimensional network structures usually produce equidimensional crystals. There are characteristic density ranges and refractive index limits in the different types corresponding to differences of structure. These and other properties easily recognized serve to distinguish one type from another, so that one can often infer the structural type from the external properties.

The term isomorphism, as here used, describes the relationship between two silicates which are structurally alike and are members of a series in which there is continuous change in the physical and chemical properties from one member to another. The term as first used (Mitscherlich 1820) had essentially this meaning. It has been modified (Tutton 1922), and used to mean simply, "having the same form," by *x*-ray crystallographers. Thus olivine and chrysoberyl have been called isomorphous. The definition given in this paper corresponds to that commonly used by mineralogists. Minerals with similar form and structure, which do not form series, may be described as isostructural (Tutton 1922).

Since two isomorphous compounds must have the same structure, they necessarily have the same number of oxygen atoms in their formulae. Likewise they must in general have the same total number of atoms, since their unit cell dimensions are usually almost alike. The atomic, or ionic, radii of most of the elements entering into the silicates do not permit of several atoms of one kind substituting for one of another without considerably changing the volume of the unit cell; substitution is, therefore, atom for atom in isomorphous compounds.

Another rule, of somewhat less importance, is that substituting atoms must be of approximately the same volume, since the structure is not much distorted in isomorphism. It is to be noted that the theory of isomorphism does not require that the substituting atoms have the same valence or chemical nature as the substituted atoms. But it is necessary that the total valence, or electrostatic charges, in the two isomorphous compounds must be the same, since they have the same number of oxygen atoms. If a divalent atom substitutes for a monvalent atom, there must be a concomitant substitution somewhere else in the structure in order that the resultant valences be the same in the two compounds. This sort of substitution is found in the plagioclase series as well as in many other silicate series.

Mixed crystals are intermediate members of an isomorphous series. The term is unsatisfactory, but no other is available, and it is generally used as defined here. Olivine $(Mg, Fe)_2SiO_4$ is a mixed crystal, the atoms of Mg and Fe being structurally equivalent. It is perhaps well to point out here that the formulae of mixed crystals are not written as if they consisted of two components, as is often done in mineralogical literature. The form $m\ Mg_2SiO_4+n\ Fe_2SiO_4$, with $m$ and $n$ as percentages, to indicate an olivine is avoided for several reasons. In the first place, the indications from structural studies (Vegard and Schjelderup 1917) point to the conclusion that Mg and Fe are statistically distributed throughout the olivine structure and there are no discrete blocks of $Mg_2SiO_4$ alongside of $Fe_2SiO_4$. Second, the adopted style of formula does not postulate the actual existence of the two end components. The ratio Mg/Fe fully expresses the part of the series to which a particular olivine belongs. To appreciate the hazards of the method of expressing the composition of mixed crystals in terms of their probable components, we can use another example from the olivine group, namely the forsterite-monticellite series. The mixed crystals have the composition $(Mg, Ca)_2SiO_4$. But $Ca_2SiO_4$ is not an end component of the series because it does not have the same structure, and no mixed crystals are found having a composition with $Ca/Mg>1$. The mistake of using probable components to express intermediate composition has led to the common practice of proposing so-called "end members" which have often no existence and thereby confuse the study of the constitution of the silicates.

When mixed crystals are known to exist from one pure component to the other, as in the forsterite-fayalite series, the series is said to be one of complete miscibility. If, however, the series is not complete and the evidence indicates that a complete miscibility is unlikely, the series is said to be one of limited miscibility. The forsterite-monticellite series is an example of limited miscibility. The conditions of limited miscibility in a series may be caused by several structural factors, according to the theory of the constitution of the silicates here given.

(1) If the substituting atoms in the series are of a volume approaching the limit of difference tolerated by the structure, only a small amount of substitution can take place, since the stability of the structure will be disturbed by the necessary distortion. This is exemplified by the universal presence of only small amounts of K in the Na silicate miner-

als. There are probably no silicates forming a complete K, Na series. The temperature at which minerals form has much to do with the degree of miscibility. In general, at a higher temperature miscibility is probably more easily accomplished because of a distended lattice. When the crystal cools, it may or may not retain its ability to carry certain elements. The phenomenon of exsolution is an expression of limited miscibility in this sense.

(2) Limited miscibility may be due to the fact that chemically like atoms, as the Mg of forsterite, are sometimes structurally in non-equivalent positions (Bragg 1930, p. 243) and it is possible for the substitution to be made in only one set of non-equivalent atoms. This is the case in the forsterite-monticellite series, where one Mg of the forsterite structure can be replaced by Ca, the other cannot without destroying the olivine type of structure, since Ca is considerably larger than Mg in ionic radius (fig. 5).

## A CLASSIFICATION BASED ON THE THEORY

The classification here proposed is based on the various types of linkage of the silicon-oxygen tetrahedra found to be the fundamental motif of the silicate structures. This is essentially a chemical classification since the composition of each type is characteristic. Within the type, structural differences introduce crystallographic variations leading to a division into families and groups. This is more or less in conformity with the older classifications now in use. In addition, certain other physical characteristics, as noted under the types, are also of value in making the broad divisions of the classification.

The major divisions here designated as structural types are perhaps not the only types possible. However, a rather careful survey of all the reliable silicate descriptions has failed to show any important group of minerals which cannot reasonably be placed in one of the types listed below.

| | |
|---|---|
| Silica type | $Z:O=1:2$ |
| Disilicate type | $Z:O=2:5$ |
| Metasilicate type | |
| Chains | $Z:O=3:8$ |
| | $Z:O=4:11$ |
| | $Z:O=1:3$ |
| Rings | $Z:O=n:3n$ |
| Pyrosilicates | $Z:O=2:7$ |
| Orthosilicates | $Z:O=1:4$ |

Z indicates the silicon-like atoms which include also Al in part, and sometimes Be in part. O refers to oxygen or oxygen-like elements such as (OH) and F, which may in rare cases replace the oxygen.

The type names here used are essentially those of the older classifications. However, according to the newer theories these names do not imply that the minerals of the types are salts of hypothetical acids. The sense in which the old names are used in this paper has already been indicated.

Within each type the broadest division is into families, wherever such division can profitably be made. Thus in the disilicates the aluminum silicates constitute a family, the divalent metal aluminum silicates constitute another, and the alkali aluminum silicates still another.

The families are further divided into groups, the members of which are more restricted in variation and more nearly alike in structure and composition and consequently in crystallographic and physical properties. The term group is used here approximately as in the standard textbooks. Groups are further divided into isomorphous series where such are evident.

The members of a series are species. These are the representatives of the series most commonly found in nature, or some convenient compositional range which includes the commonly occurring members of the series. The term species is also applied to minerals that, so far as known, have fixed compositions; such species are nearly all rare silicates that have been found but once and therefore we have no evidence of their variability. Surprisingly few silicates have no important variation in composition. Species are then either members of a series, or of fixed composition. In either case, they are the smallest important unit of our classification. In the silicates it is generally true that species are members of a series; and it is for this reason that the writer regards the series as the most important unit of the classification. In the sense that species are arbitrary segments of a series they are not the natural units in the silicates. When one has completely described a series, one has at the same time described all of the species of that series. Undue emphasis in the past on the minute variations of a series and the too profuse naming of these variants have encumbered the literature of the silicates with many insignificant names. If many of these are not found in our classification, it is not because they have not been considered; but because, according to the writer's views, they would only obscure the pertinent data.

Corresponding to the divisions of the classification the formulae are progressively less generalized, beginning with the type formula, where it is feasible to write one, and ending with that of the series or the species.

Each formula of a more general nature embraces all of the succeeding formulae. In many of the types a general formula defining the type must be so generalized that little profit is gained by giving it. On the other hand, a type formula of the silica type gives a clear picture of all the members. Accordingly, a completely consistent procedure cannot well be followed. Where clarity is gained, all the formulae will be given.

As an example of the method of treatment in the study of a silicate to determine its constitution, the amphiboles will be used, for several reasons. (1) They are perhaps the most complex chemical compounds among the silicates. (2) They afford a good example of groups containing many series which show various types of chemical complexity.

The amphiboles are a well-studied group chemically. Literally hundreds of analyses exist. The first step in the study consisted of determining the ratios of the various atoms (and possible groups of atoms) to each other, assuming that a constant number of oxygen atoms are in the formulae of all amphiboles. From the structural study (Warren 1929) a clear picture of the relation between the atoms is obtained. Tremolite, which was studied in detail by Warren, has 44 oxygens and 4 hydroxyls in the unit cell. Assuming that the same holds for all the amphiboles, their analyses were computed on that basis. The analyses as given in the literature are in the oxide form. It is necessary, however, to express the analysis in terms of metals and oxygen, because in our studies atomic relations are important, and the oxide form frequently masks the true relations. The method of treating the analysis is as follows. Taking as an example riebeckite from Pike's Peak, Colorado, as analysed by Kunitz (1930), we have a division into six columns as given.

Table 2. Discussion of a Hornblende Analysis

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 49.46 | 0.820 | 1.640 | 0.820 | 7.9 | 8.0 |
| $Al_2O_3$ | 1.05 | 0.010 | 0.030 | 0.020 | 0.2 | 2.1 |
| $Fe_2O_3$ | 15.78 | 0.099 | 0.297 | 0.198 | 1.9 | |
| $FeO$ | 21.03 | 0.292 | 0.292 | 0.292 | 2.8 | 3.1 |
| $MgO$ | 0.62 | 0.015 | 0.015 | 0.015 | 0.1 | |
| $MnO$ | 1.23 | 0.017 | 0.017 | 0.017 | 0.2 | |
| $Na_2O$ | 8.19 | 0.132 | 0.132 | 0.264 | 2.6 | 2.9 |
| $K_2O$ | 1.72 | 0.018 | 0.018 | 0.036 | 0.3 | |
| $H_2O$ | 1.15 | 0.064 | 0.064 | 0.128 | 1.2 | 1.2 |
| | 100.23 | | 2.506<br>f=9.58 | | | |

1. The percentage composition expressed in terms of the oxide.
2. The molecular ratio.
3. The oxygen atoms of the ratio given in 2; each ratio in column 2 is multiplied by the number of oxygen atoms in the corresponding oxide.
4. The positive atoms in the ratio in column 2, each multiplied by the number of positive atoms in the corresponding oxide. If by *x*-ray analysis the dimensions and molecular weight of the unit cell have been determined, the atomic contents of the cell may be directly computed from column 4 by multiplying each term by the molecular weight of the unit cell.
5. The total of the oxygen atoms in column 3 is multiplied by a factor f, in order to bring that total to the required oxygen number, in this case 24. This same factor f is used to multiply each ratio of column 4 to obtain the values in column 5.
6. Structurally equivalent, or isomorphous groups of atoms are combined to yield the formula; in this case $(Na, K)_3(Fe'', Mg, Mn)_3(Fe''', Al)_2(Al, Si)_8O_{23}(OH)$.

The formula here given is half the content of the unit cell. It is often possible to discuss the constitution of a series by using a small fraction of the true unit and thereby simplify the formula. However, there is often a necessity to use the full cell contents, no matter how large, in order to grasp the full significance of the variations in a complex series. Precisely the same procedure is followed for all the analyses which in the author's opinion are complete and made on fairly pure material. The study yields a general formula for the amphibole group, as follows:

$$(WXY)_{7-8}(Z_4O_{11})_2(O, OH, F)_2$$

with W = Ca; Na, K in minor amount, and sometimes Li.
X = Mg, Fe″, Mn″, Al in part.
Y = Al, Fe‴, Ti, principally.
Z = Si principally and Al in part.

The symbols W, X, Y, Z are used throughout the classification to indicate atoms of the same kind, namely atoms having given ionic radii and co-ordination numbers. The W atoms are mainly the alkalies and Ca, Ba, Sr; the X atoms are divalent atoms for the most part, having intermediate radii and large co-ordination numbers; the Y atoms are trivalent or tetravalent with generally smaller ionic radii. The Z atoms are predominantly Si, with some Al in certain silicates, such as the amphiboles. The Z atoms are of small radius and have the co-ordination number 4.

A further study of the amphiboles showed that there are probably four major series comprising the group. These series are:

The anthophyllite series—$X_7(Z_4O_{11})_2(OH)_2$; with X = Mg, Fe and Mg/Fe large; Ca subordinate; Z = Si almost entirely; Al sometimes in small amounts.

The cummingtonite series—$X_7(Z_4O_{11})_2(OH)_2$; X = Mg, Fe″. Mn and Zn subordinate; Al in minor amounts; Z = Si predominant, Al sometimes in small amounts.

Tremolite-actinolite series—$W_2X_5(Z_4O_{11})_2(OH)_2$; W = Ca predominantly, Na in minor amount; X = Mg, Fe″, with some Al; Z = Si predominantly, Al in minor amount.

Hornblende series—$W_3(X, Y)_5(Z_4O_{11})_2(OH, F)_2$

| X | Y | Z = Si:Al | Species |
|---|---|---|---|
| 5 | 0 | 7:1 | Hornblende-edenite |
| 4 | 1 | 6:2 | Hastingsite |
| 3 | 2 | 8:0 | Glaucophane |
| 4 | 1 | 8:0 | Arfvedsonite |

W = Ca, Na with Ca never greater than 2 in formula; Li rare (in holmquistite); K in subordinate amounts. X = Mg, Fe″, Mn″; Y = Al, Fe‴, Ti; Z = Si, Al, in ratios given above.

It is to be noted that the general group formula is such that the formulae of the series may be derived from it. The series formulae give the general variations within a specified range and show the character of that variation. In the regular classification a list of the species, with specific formulae, corresponding to some part of the series, is given. This is the method of presenting the data.

## II. A TABULATED ARRANGEMENT OF THE SILICATES ACCORDING TO THE NEW CLASSIFICATION

### Silica Type $W(Z_rO_{2r})\cdot N$

W = Ca, Na, K; Li, Cs rare; Mn, Fe, Zn very rare; Z = Si, Al; Be rare; N = S, Cl, $CO_3$, $SO_4$, and in the zeolites $H_2O$.

| | |
|---|---|
| *Silica group:* | $SiO_2$ |
| *Petalite group:* | $WZ_5O_{10}$ |
| Petalite | $(Li, Na)AlSi_4O_{10}$ |
| Milarite | $(Ca, K)(Al, Be, Si)_5O_{10}$ |
| Leifite | $Na_4Al_2Si_9O_{22}F_2$ |
| *Feldspar group:* | $WZ_4O_8$ |
| *Monoclinic members:* | |
| Orthoclase | $KAlSi_3O_8$ |
| Soda-orthoclase | $(K, Na)AlSi_3O_8$ |
| Hyalophane | $(K, Na, Ba)Al(Al, Si)Si_2O_8$ |
| Celsian | $BaAl_2Si_2O_8$ |
| *Triclinic members:* | |
| *Microcline series:* | $(K, Na)AlSi_3O_8$ |
| Microcline | $KAlSi_3O_8$ |
| Soda-microcline | $(K, Na)AlSi_3O_8$ |
| Anorthoclase | $(Na, K)AlSi_3O_8$ |
| *Plagioclase series:* | $(Na, Ca)Al(Al, Si)Si_2O_8$ |
| Albite | $NaAlSi_3O_8$ |

| | |
|---|---|
| Labradorite | $(Na, Ca)Al(Al, Si)Si_2O_8$ |
| Anorthite | $CaAl_2Si_2O_8$ |
| Anemousite | $(Na, Ca, Na_2)Al(Al, Si)Si_2O_8$ |
| Pollucite | $W_4Z_{13}O_{26}\cdot H_2O$ |
| Leucite | $WZ_3O_6$ |
| *Nephelite group:* | $WZ_2O_4$ |
| Nephelite | $(Na, K)(Al, Si)_2O_4$ |
| Kaliophilite | $(K, Na)(Al, Si)_2O_4$ |
| Eucryptite | $Li(Al, Si)_2O_4$ |
| *Cancrinite group:* | $W_{6-8}Z_{12}O_{24}N_{1-2}\cdot 2\text{–}3H_2O$ |
| Cancrinite | $(Na, K)_{6-8}Al_6Si_6O_{24}\cdot (CO_3)_{1-2}\cdot 2\text{–}3H_2O$ |
| Microsommite | $(Na, Ca, K)_8Al_6Si_6O_{24}\cdot (Cl, SO_4)_3$ |
| Davyne | |
| *Sodalite group:* | $W_{8\pm}Z_{12}O_{24}\cdot N_{1-2}$ |
| Sodalite | $Na_8Al_6Si_6O_{24}\cdot Cl_2$ |
| Hackmanite | $Na_8Al_6Si_6O_{24}\cdot (Cl, S)_2$ |
| Noselite | $Na_8Al_6Si_6O_{24}\cdot SO_4$ |
| Hauyne | $(Na, Ca)_{6-8}Al_6Si_6O_{24}\cdot (SO_4)_{1-2}$ |
| Lazurite | $Na_{8-10}Al_6Si_6O_{24}\cdot S_{2\pm}$ |
| Helvite | $(Mn, Fe)_8Be_6Si_6O_{24}\cdot S_2$ |
| Danalite | $(Mn, Fe, Zn)_8Be_6Si_6O_{24}\cdot S_2$ |
| *Scapolite series:* | $W_4Z_{12}O_{24}\cdot N$ |
| Marialite | $(Na, Ca)_4Al_3(Al, Si)_3Si_6O_{24}(Cl, CO_3, SO_4)$ |
| Meionite | $(Ca, Na)_4Al_3(Al, Si)_3Si_6O_{24}(Cl, CO_3, SO_4)$ |
| Zeolite Family | $W_mZ_rO_{2r}\cdot sH_2O$ |
| *Mordenite series:* | $(Ca, Na, K)_{5-7}Al_7(Al, Si)Si_{32}O_{80}\cdot 22H_2O$ |
| *Heulandite group:* | |
| Clinoptilolite | $Ca_2Na_3Al_7Si_{33}O_{80}\cdot 23H_2O$ |
| Heulandite | $(Ca, Na, K)_6Al_{10}(Al, Si)Si_{29}O_{80}\cdot 25H_2O$ |
| Epistilbite | $Ca_5NaAl_{11}Si_{29}O_{80}\cdot 25H_2O$ |
| Brewsterite | $(Ca, Ba, Sr)_5NaAl_{11}Si_{29}O_{80}\cdot 25H_2O$ |
| *Stilbite group:* | |
| Stilbite | $(Ca, Na, K)_6Al_{10}(Al, Si)_2Si_{28}O_{80}\cdot 30H_2O$ |
| Epidesmine | $(Ca, Na)_6Al_{10}(Al, Si)_2Si_{28}O_{80}\cdot 30H_2O$ |
| Harmotome | $Ba_5(Na, K)Al_{11}Si_{29}O_{80}\cdot 25H_2O$ |
| Phillipsite | $(Ca, Ba, K, Na)_{12}Al_{16}(Al, Si)_4Si_{20}O_{80}\cdot 30\text{–}40H_2O$ |
| Wellsite | $(Ca, Ba, Sr, K, Na)_{12}Al_{16}(Al, Si)_4Si_{20}O_{80}\cdot 30\text{–}40H_2O$ |
| Gismondite | $(Ca, K)_{10}Al_{17}(Al, Si)_2Si_{21}O_{80}\cdot 36\text{–}40H_2O$ |
| Erionite | $Ca(Na, K)Al_4Si_{12}O_{32}\cdot 12H_2O$ |
| Stellerite | $CaAl_2Si_7O_{18}\cdot 7H_2O$ |
| *Chabazite group:* | |
| Chabazite | $(Ca, Na, K)_7Al_{12}(Al, Si)_2Si_{26}O_{80}\cdot 40H_2O$ |
| Gmelinite | $(Na, Ca)_{12}Al_{12}(Al, Si)_2Si_{26}O_{80}\cdot 40H_2O$ |

| | |
|---|---|
| Levynite | $Ca_8Al_{16}Si_{24}O_{80} \cdot 40H_2O$ |
| *Thomsonite group:* | |
| Thomsonite | $(Ca, Na)_{12}Al_{16}(Al, Si)_4Si_{20}O_{80} \cdot 24H_2O$ |
| Gonnardite | $Ca_4Na_8Al_{16}Si_{24}O_{80} \cdot 28H_2O$ |
| Arduinite | $(Ca, Na)_{12}Al_{16}(Al, Si)Si_{23}O_{80} \cdot 29H_2O$ |
| Ashcroftine | $(Ca, Mg)_5(K, Na)_8Al_{18}Si_{22}O_{80} \cdot 35H_2O$ |
| *Natrolite group:* | |
| Natrolite | $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ |
| Mesolite | $Ca_2Na_2Al_6Si_9O_{30} \cdot 8H_2O$ |
| Scolecite | $CaAl_2Si_3O_{10} \cdot 3H_2O$ |
| Edingtonite | $BaAl_2Si_3O_{10} \cdot 4H_2O$ |
| *Miscellaneous zeolites:* | |
| Faujasite | $CaNa_2Al_4Si_{10}O_{28} \cdot 20H_2O$ |
| Analcite | $NaAlSi_2O_6 \cdot H_2O$ |
| Laumontite | $(Ca, Na)_7Al_{12}(Al, Si)_2Si_{26}O_{80} \cdot 25H_2O$ |
| Ferrierite | $Mg_2Na_4Al_8Si_{32}O_{80} \cdot 20H_2O$? |
| *Doubtful species:* | |
| Laubanite | $Ca_2Al_2Si_5O_{15} \cdot 6H_2O$ |
| Didymolite | $Ca_2Al_6Si_8O_{27}$ |
| Dachiardite | composition doubtful |

| | |
|---|---|
| Cordierite | $(Mg, Fe, Mn)_2(Al, Fe)_4Si_5O_{18} \cdot H_2O$ |

DISILICATE TYPE

| ALUMINUM DISILICATES: | *p* | *s* | $Y_pSi_4O_{10}(OH)_{3p-4} \cdot sH_2O$ |
|---|---|---|---|
| Pyrophyllite | 2 | 0 | $Al_2Si_4O_{10}(OH)_2$ |
| Anauxite | 2⅔ | 1 | $Al_8(Si_4O_{10})_3(OH)_{12} \cdot 3H_2O$ |
| Kaolin group | 4 | 0–2 | $Al_4Si_4O_{10}(OH)_8$ |
| Canbyite | 4 | 4 | $Fe_4'''Si_4O_{10}(OH)_8 \cdot 4H_2O$ |
| Batchelorite | 4 | *s** | $Al_4Si_4O_{10}(OH)_8 \cdot sH_2O$ |
| Beidellite | 2⅔ | 4 | $Al_8(Si_4O_{10})_3(OH)_{12} \cdot 12H_2O$ |

NON-ALUMINUM DISILICATES:

| | |
|---|---|
| *Talc group:* | |
| Talc | $Mg_3Si_4O_{10}(OH)_2$ |
| *Antigorite series:* | $X_6Si_4O_{10}(OH)_8$ |
| Antigorite | $Mg_6Si_4O_{10}(OH)_8$ |
| Nepouite | $(Mg, Ni)_6Si_4O_{10}(OH)_8$ |

| | |
|---|---|
| Connarite | $(Ni, Mg)_8(Si_4O_{10})_3(OH)_4 \cdot 6H_2O$ |
| *Freidelite group:* | $X_nSi_6O_{15}(OH, F, Cl)_{2(n-3)}sH_2O$ |
| Zeophyllite | $Ca_3Si_6O_{10}(OH, F)_{10}$ |
| Friedelite | $Mn_8Si_6O_{15}(OH, Cl)_{10}$ |
| Pyrosmalite | $(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}$ |
| Schallerite | $Mn_8(Si, As)_6O_{15}(OH, Cl)_{10-}$ |

| | |
|---|---|
| Ferroschallerite | $(Fe, Mn)_8(Si, As)_6O_{15}(OH, Cl)_{10}$– |
| Centrallassite | $Ca_4Si_6O_{15}(OH)_2\cdot 5H_2O$ |
| Truscottite | $(Ca, Mg)_4Si_6O_{15}(OH)_2\cdot 5H_2O$ |
| Gyrolite | $(Ca_4Si_6O_{15}(OH)_2\cdot 3H_2O$ |

*Miscellaneous non-aluminum disilicates:*

| | |
|---|---|
| Bementite | $Mn_5Si_4O_{10}(OH)_6$ |
| Errite | $Mn_4Si_4O_{10}(OH)_4\cdot 3H_2O$ |
| Apophyllite | $Ca_4K(Si_4O_{10})F_2\cdot 8H_2O$ |
| Okenite | $Ca_2(Si_4O_{10})\cdot 4H_2O$ |

ANHYDROUS NON-ALUMINUM DISILICATES:

| | |
|---|---|
| | $X_n(Si_4O_{10})$ |
| Gillespite | $BaFeSi_4O_{10}$ |
| Sanbornite | $Ba_2Si_4O_{10}$ |

| | |
|---|---|
| CHLORITE FAMILY: | $X_nZ_4O_{10}(OH)_{2(n-2)}\cdot sH_2O$ |
| *Chlorite group:* | $(Mg, Fe)_{6-p}(Al, Fe''')_{2p}Si_{4-p}O_{10}(OH)_8$ |
| *Leptochlorite group:* | $(Mg, Fe)_{n-p}(Al, Fe''')_{2p}Si_{4-p}O_{10}(OH)_{2(n-2)}\cdot sH_2O$; $5.5>n>4; 2>p>0.7$ |
| *Vermiculite group:* | $(Mg, Fe'')_{n-p}(Al, Fe''')_{2p}Si_{4-p}O_{10}(OH)_{2(n-2)}\cdot sH_2O$ |

| | $n$ | $p$ | $s$ |
|---|---|---|---|
| Vermiculite | 4 | 0.80 | 4 |
| Saponite | 3.64 | 0.36 | 4 |
| Griffithite | 3.5 | 0.67 | 3.5 |
| Roseite | 3 | 1.33 | 4 |

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BRITTLE MICA FAMILY: $(Mg, Ca, Fe'', Mn)_{n-p}(Al, Fe''')_{2p}Si_{4-p}O_{10}(OH)_{2(n-2)}\cdot sH_2O$

| | $n$ | $p$ |
|---|---|---|
| Chalcodite | 3 | 4/10 |
| Epichlorite | $3\frac{1}{4}$ | $\frac{3}{4}$ |
| Stilpnomelane | 2 | 1 |
| Ottrellite | $2–2\frac{1}{2}$ | $1\frac{1}{2}–1$ |
| Margarite | 3 | 2 |
| Ephesite | 4 | 2 |
| Prehnite | 3 | 1 |
| Chloritoid | 4 | 2 |

| | |
|---|---|
| Clintonite | $X_4Z_4O_{10}(OH)_2$ |

| | |
|---|---|
| *Mica group:* | $W(X, Y)_{2-3}Z_4O_{10}(O, OH, F)_2$ |
| *Muscovite series* | $(K, Na)(Al, Mg, V)_2(Si, Al)_4O_{10}(OH)_2$ |
| *Biotite series* | $K(Mg, Fe'', Al)_3(Si, Al)_4O_{10}(O, OH)_2$ |
| *Lithia mica series* | $K(Mg, Fe'', Mn, Li, Al, Fe''')_3(Si, Al)_4O_{10}(O, OH, F)_2$ |

*Miscellaneous disilicates:*

| | |
|---|---|
| *Glauconite* | $K_2(Mg, Fe)_2Al_6(Si_4O_{10})_3(OH)_{12}$ |
| Pholidolite | $KMg_6AlSi_7O_{20}(OH)_4\cdot 3H_2O$ |
| Cookeite | $(Li, Al)_4(Si, Al)_4O_{10}(OH)_4\cdot 2H_2O$ |

| | |
|---|---|
| Bityite | $Ca_4(Li, Be, Al)_{12}[(Si, Al)_4O_{10}]_3(OH)_{20}$ |
| Ganophyllite | $NaMn_6Al_2(Si_4O_{10})_2(OH)_{11}$ |

### Metasilicate Type

**Chain Structures:**

| | |
|---|---|
| *Amphibole group:* | $(W, X Y)_{7-8}(Z_4O_{11})_2(O, OH, F)_2$ |
| *Anthophyllite series:* | $X_7(Z_4O_{11})_2(OH)_2$ |
| Anthophyllite | $(Mg, Fe)_7Si_8O_{22}(OH)_2$ |
| Gedrite | $(Mg, Fe, Al)_7(Al, Si)_8O_{22}(OH)_2$ |
| *Cummingtonite series:* | $X_7(Z_4O_{11})_2(OH)_2$ |
| Cummingtonite | $(Mg, Fe)_7Si_8O_{22}(OH)_2$ |
| Grünerite | $(Mg, Fe, Mn)_7Si_8O_{22}(OH)_2$ |
| *Tremolite-actinolite series:* | $W_2X_5(Z_4O_{11})_2(OH)_2$ |
| Tremolite | $Ca_2Mg_5Si_8O_{22}(OH)_2$ |
| Actinolite | $Ca_2(Mg, Fe)_5Si_8O_{22}(OH)_2$ |
| *Hornblende series:* | $2W_3(X, Y)_5(Z_4O_{11})_2(O, OH, F)_2$ |
| Edenite | $Ca_4Na_2Mg_{10}Al_2Si_{14}O_{44}(OH, F)_4$ |
| Pargasite | $Ca_4Na_2Mg_9Al_4Si_{13}O_{44}(OH, F)_4$ |
| Hastingsite | $Ca_4Na_2Mg_8Al_6Si_{12}O_{44}(OH, F)_4$ |
| Hornblende | $Ca_4Na_2(Mg, Fe'')_8(Al, Fe''', Ti)_6Si_{12}O_{44}(O, OH)_4$ |
| Kearsutite | $Ca_4Na_1(Mg, Fe'')_7(Al, Fe''')_5Ti_2Si_{12}O_{46}(OH)_2$ |
| Arfvedsonite | $Na_6Mg_8Al_2Si_{16}O_{44}(OH, F)_4$ |
| Arfvedsonite | $Ca_2Na_4Fe_7''(Al, Fe''')_6Si_{13}O_{44}(OH)_4$ |
| Holmquistite | $CaNaLi_2Mg_6Al_5Si_{15}O_{44}(OH)_4$ |
| Glaucophane | $Na_4Mg_6Al_4Si_{16}O_{44}(OH, F)_4$ |
| Riebeckite | $Na_6Fe_6''Fe_4'''Si_{16}O_{46}(OH)_2$ |
| Narsarsukite | $Na_2(Ti, Fe''')Si_4(O, F)_{11}$; Ti:Fe=3:1 |
| Chrysotile | $(Mg, Fe)_6Si_4O_{11}(OH)_6 \cdot H_2O$ |
| *Pyroxene group:* | $W(X, Y)(Z_2O_6)$ |
| *Enstatite series:* | $WXZ_2O_6$ |
| Enstatite | $Mg_2Si_2O_6$ |
| Hypersthene | $(Mg, Fe)_2Si_2O_6$ |
| *Pigeonite series:* | $WXZ_2O_6$ |
| Clinoenstatite | $Mg_2Si_2O_6$ |
| Pigeonite | $(Ca, Mg)(Mg, Fe)Si_2O_6$ |
| *Diopside series:* | $W(X, Y)Z_2O_6$ |
| Diopside | $CaMgSi_2O_6$ |
| Hedenbergite | $CaFeSi_2O_6$ |
| Augite | $Ca(Mg, Fe, Al)(Al, Si)_2O_6$ |
| Schefferite | $Ca(Mg, Fe, Mn)Si_2O_6$ |
| Zinc schefferite | $Ca(Mg, Mn, Zn)Si_2O_6$ |
| Jeffersonite | $Ca(Mg, Mn, Fe, Zn)Si_2O_6$ |
| *Acmite-jadeite series:* | $WYZ_2O_6$ |
| Acmite | $NaFe'''Si_2O_6$ |

| | |
|---|---|
| Jadeite | $NaAlSi_2O_6$ |
| Aegirite | $(Ca, Na)(Mg, Fe''', Al)Si_2O_6$ |
| Spodumene | $LiAlSi_2O_6$ |
| PYROXENOID FAMILY: | |
| *Rhodonite series:* | $WXZ_2O_6$ |
| Rhodonite | $(Mn, Ca)MnSi_2O_6$ |
| Fowlerite | $(Mn, Ca)(Mn, Zn)Si_2O_6$ |
| Iron rhodonite | $(Mn, Ca)(Mn, Fe)Si_2O_6$ |
| Pyroxmangite | $Mn(Mn, Fe)Si_2O_6$ |
| Sobralite | $(Mn, Ca)(Mg, Fe)Si_2O_6$ |
| *Wollastonite group:* | $W_3X_3Z_6(O, OH)_{18}$ |
| Wollastonite | $Ca_3Ca_3Si_6O_{18}$ |
| Bustamite | $Ca_3Mn_3Si_6O_{18}$ |
| Pectolite | $Ca_4Na_2Si_6O_{16}(OH)_2$ |
| Schizolite | $(Ca, Mn)_4Na_2Si_6O_{16}(OH)_2$ |
| Alamosite | $Pb_3Pb_3Si_6O_{18}$ |
| *Miscellaneous pyroxenoids:* | |
| Margarosanite | $(Pb, Ca, Mn)SiO_3$ |
| Babingtonite | $Ca_2Fe''Fe'''Si_5O_{14}(OH)$ |
| Taramellite | $Ba_2Fe_2'''Si_5O_{15}$ |
| Hyalotekite | $(Ba, Ca, Pb)_4BSi_6O_{17}(F, OH)$ |
| Neptunite | $(Na, K)(Fe'', Mn'', Ti)Si_2O_6$ |
| CALCIUM METASILICATE FAMILY: | |
| Xonotlite | $Ca_3Si_3O_8(OH)_2$ |
| Inesite | $(Ca, Mn)_3Si_3O_8(OH)_2$ |
| Hillebrandite | $Ca_2SiO_3(OH)_2$ |
| Riversideite | $Ca_2Si_2O_6 \cdot H_2O$ |
| Jurupaite | $(Ca, Mg)_2Si_2O_6 \cdot H_2O$ |
| Crestmoreite | $CaSiO_3 \cdot 2H_2O$ |
| Radiophyllite | $CaSiO_3 \cdot H_2O$ |
| Afwillite | $Ca_3Si_2O_6(OH)_2 \cdot 2H_2O$ |
| COPPER METASILICATE FAMILY: | $CuSiO_3 \cdot sH_2O$ |
| Chrysocolla | $CuSiO_3 \cdot 2H_2O$ |
| Bisbeeite | $CuSiO_3 \cdot H_2O$ |
| Shattuckite | $2(CuSiO_3) \cdot H_2O$ |
| Plancheite | $3(CuSiO_3) \cdot H_2O$ |
| *Miscellaneous metasilicates:* | |
| Carpholite | $MnAl_2(SiO_3)_2(OH)_4$ |
| Stokesite | $CaSn(SiO_3)_3 \cdot 2H_2O$ |
| Searlesite | $NaB(SiO_3)_2 \cdot H_2O$ |
| Bavenite | $Ca_4BeAl_2Si_9O_{25}(OH)_2$ |
| Cenosite | $Ca_2(Ce, Y)_2(SiO_3)_4 \cdot CO_3 \cdot H_2O$ |
| Eudidymite | $H_2Na_2Be_2(Si_3O_8)_2$ |

| | |
|---|---|
| Epididymite | $H_2Na_2Be_2(Si_3O_8)_2$ |
| Elpidite | $H_2Na_2Zr(Si_3O_8)_2\cdot H_2O$ |
| Leucosphenite | $BaNa_2(Ti, Zr)(Si_3O_8)_2$ |
| Ussingite | $Na_2Al(Si_3O_8)(OH)$ |

**Ring Structures:**

| | |
|---|---|
| Benitoite | $BaTiSi_3O_9$ |
| *Catapleiite series:* | |
| Catapleiite | $(Na_2, Ca)ZrSi_3O_9\cdot 2H_2O$ |
| Natron-catapleiite | $Na_2ZrSi_3O_9\cdot 2H_2O$ |
| Eudialyte (eucolite) | $(Ca, Na)_2(Zr, Ce, Fe'', Mn)Si_3O_8(OH, Cl)$ |
| Steenstrupine | $(Ca, Na)_4Mn(Ce, La, Al, Fe''')_6(Si, Ti)_9O_{27}(OH)_7\cdot 3H_2O$ |
| *Tourmaline series:* | $WX_3Y_6(Z_3O_9)_3(O, OH, F)_4$ |
| Dravite | $NaMg_3B_3Al_3(Al_3Si_6O_{27})(OH)_4$ |
| Ca-tourmaline | $CaMg_3B_3Al_3(Al_3Si_6O_{27})(O, OH)_4$ |
| Indicolite | $Na(Al, Fe'', Li, Mg)_3B_3Al_3(Al_3Si_6O_{27})(O, OH, F)_4$ |
| Tourmaline | $(Na, Ca)(Mg, Fe'', Fe''')_3B_3Al_3(Al_3Si_6O_{27})(O, OH)_4$ |
| "Schorl" | $NaFe_3B_3Al_3(Al_3Si_6O_{27})(OH)_4$ |
| Beryl | $Al_2Be_3Si_6O_{18}$ |

### Pyrosilicate Type

| | |
|---|---|
| *Thalenite group:* | |
| Thalenite | $Y_2Si_2O_7$ |
| Thortvietite | $(Sc, Y)_2Si_2O_7$ |
| Cerite | $(Ce, Y, Pr, Nd)_2Si_2O_7\cdot H_2O$ |
| Rowlandite | $(Y, Ce, La)_4Fe''(Si_2O_7)_2\cdot F_2$ |
| *Melilite group:* | |
| *Melitite series:* | $W_2(X, Y)Z_2O_7$ |
| Åkermanite | $Ca_2MgSi_2O_7$ |
| Gehlenite | $Ca_2Al(AlSiO_7)$ |
| Soda-melilite | $CaNaAlSi_2O_7$ |
| Hardystonite | $Ca_2ZnSi_2O_7$ |
| Leucophanite | $CaNaBeSi_2O_6F$ |
| Meliphanite | $(Ca, Na)_2Be(Al, Si)_2O_6F$ |
| *Barysilite group:* | |
| Barysilite | $Pb_3Si_2O_7$ |
| Ganomalite | $(Ca, Pb)_{10}(Si_2O_7)_3(OH)_2$ |
| Nasonite | $(Ca, Pb)_{10}(Si_2O_7)Cl_2$ |

HEMIMORPHITE FAMILY:

| | |
|---|---|
| Hemimorphite | $Zn_4Si_2O_7(OH)_2\cdot H_2O$ |
| Clinohedrite | $Ca_2Zn_2Si_2O_7(OH)_2\cdot H_2O$ |
| Bertrandite | $Be_4Si_2O_7(OH)_2$ |
| Cuspidine | $Ca_4Si_2O_7F_2$ |
| Molybdophyllite | $Pb_2Mg_2Si_2O_7(OH)_2$ |
| Murmanite | $Na_2Ti_2Si_2O_7(OH)_4$ |

| | |
|---|---|
| *Miscellaneous pyrosilicates:* | |
| Barylite | $BaBe_2Si_2O_7$ |
| Lawsonite | $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$ |
| Harstigite | $(Ca, Mn, Mg)_8Al_2(Si_2O_7)_3(OH)_4$ |
| Danburite | $CaB_2(Si_2O_7)O$ |
| Astrophyllite | $(Na, Ca)_5(Fe'', Al, Ti)_{15}(Si_2O_7)_6(F, OH)_8$ |
| Aenigmatite | $(Na, Ca)_4(Fe'', Mn, Fe''', Ti, Al)_{13}(Si_2O_7)_6$ |

## ORTHOSILICATES

**Normal Orthosilicates:**

| | |
|---|---|
| *Chrysolite group:* | $X_2SiO_4$ |
| *Olivine series:* | $(Ca, Mn, Mg, Fe, Pb)(Mg, Fe, Mn, Zn)SiO_4$ |
| Forsterite | $Mg_2SiO_4$ |
| Olivine | $(Mg, Fe)_2SiO_4$ |
| Hortonolite | $(Mg, Fe, Mn)_2SiO_4$ |
| Knebelite | $(Fe, Mn)_2SiO_4$ |
| Fayalite | $Fe_2SiO_4$ |
| Tephroite | $(Mn, Zn, Mg)_2SiO_4$ |
| Roepperite | $(Fe, Mn, Zn)_2SiO_4$ |
| Glaucochroite | $CaMnSiO_4$ |
| Monticellite | $CaMgSiO_4$ |
| Larsenite | $PbZnSiO_4$ |
| Calcium larsenite | $(Pb, Ca)ZnSiO_4$ |

| | |
|---|---|
| Larnite | $Ca_2SiO_4$ |
| Merwinite | $Ca_3Mg(SiO_4)_2$ |

| | |
|---|---|
| *Phenakite group:* | $X_2SiO_4$ |
| Phenacite | $Be_2SiO_4$ |
| Willemite | $Zn_2SiO_4$ |
| Troostite | $(Zn, Mn)_2SiO_4$ |
| Trimerite | $(Mn, Ca)BeSiO_4$ |
| Dioptase | $H_2CuSiO_4$ |

| | |
|---|---|
| *Humite group:* | $X_{2r+1}(SiO_4)_r(OH, F)_2$ |
| Norbergite | $Mg_3(SiO_4)_1(OH, F)_2$ |
| Chondrodite | $Mg_5(SiO_4)_2(OH, F)_2$ |
| Humite | $Mg_7(SiO_4)_3(OH, F)_2$ |
| Clinohumite | $Mg_9(SiO_4)_4(OH, F)_2$ |

| | |
|---|---|
| *Hodgkinsonite group:* | $X_{2r+1}(SiO_4)_r(OH, F)_2$ |
| Hodgkinsonite | $(Zn_2Mn)(SiO_4)(OH)_2$ |
| Alleghanyite | $Mn_5(SiO_4)_2(OH, F)_2$ |
| Leucophoenicite | $Mn_7(SiO_4)_3(OH)_2$ |

| | |
|---|---|
| Gageite | $(Mn, Mg, Zn)_{16}(SiO_4)_6(OH)_8 \cdot 3H_2O$ |

*Garnet group:* $X_3Y_2(ZO_4)_3$; X = Mg, Fe, Mn, Ca; Y = Al, Fe''', Cr, Ti, Mn'''; Z = Si, Ti in subordinate amount.

| | |
|---|---|
| *Almandite series:* | $(Mg, Fe, Mn)_3Al_2(SiO_4)_3$ |
| Pyrope | $Mg_3Al_2(SiO_4)_3$ |
| Almandite | $Fe_3Al_2(SiO_4)_3$ |
| Spessartite | $Mn_3Al_2(SiO_4)_3$ |
| *Andradite series:* | $Ca_3(Al, Fe, Cr)_2(SiO_4)_3$ |
| Grossularite | $Ca_3Al_2(SiO_4)_3$ |
| Andradite | $Ca_3Fe_2(SiO_4)_3$ |
| Uvarovite | $Ca_3Cr_2(SiO_4)_3$ |
| Titanium garnet | $Ca_3(Al, Fe'', Fe''', Ti)_2[(Si, Ti)O_4]_3$ |
| Sarcolite | $(Ca, Na_2)_3Al_2(SiO_4)_3$ |
| Vesuvianite | $Ca_{10}Al_4(Mg, Fe)_2Si_9O_{34}(OH)_4$ |
| *Epidote group:* | $W_2Y_3(ZO_4)_3(OH)$ |
| Zoisite | $Ca_2Al_3(SiO_4)_3(OH)$ |
| *Epidote series:* | $(Ca, Mn)_2(Al, Fe, Mn)_3(SiO_4)_3(OH)$ |
| Clinozoisite | $Ca_2Al_3(SiO_4)_3(OH)$ |
| Epidote | $Ca_2(Al, Fe)_3(SiO_4)_3(OH)$ |
| Piedmontite | $Ca_2(Al, Fe, Mn)_3(SiO_4)_3(OH)$ |
| Manganepidote | $(Ca, Mn'')_2(Al, Mn''')_3(SiO_4)_3(OH)$ |
| *Allanite series:* | |
| Allanite | $(Ca, Ce, La, Na)_2(Al, Fe, Mn, Be, Mg)_3(SiO_4)_3(OH)$ |
| Magnesium orthite | $CaCeMg_2Al[Si(O, OH)_4]_3F$ |
| Nagatelite | $(Ca, Ce)_2(Al, Fe''', Fe'')_3[(P, Si)O_4]_3(OH)$ |
| Hancockite | $(Ca, Pb, Sr, Mn)_2(Al, Fe, Mn)_3(SiO_4)_3(OH)$ |
| Pumpellyite | $Ca_2Al_3(SiO_4)_3(OH)\cdot H_2O$ |
| *Zircon group:* | $XSiO_4$ |
| Zircon | $ZrSiO_4$ |
| Thorite | $ThSiO_4$ |
| WÖHLERITE FAMILY: | |
| *Wöhlerite group* | $W_3X(ZO_4)_2(F, OH)$ |
| Rosenbuschite | $(Na, Ca)_3(Fe, Ti, Zr)(SiO_4)_2F$ |
| Wöhlerite | $(Ca, Na)_3(Zr, Cb)(SiO_4)_2F$ |
| Hiortdahlite | $(Ca, Na)_3(Fe, Mn, Zr, Ti)(SiO_4)_2(F, OH)$ |
| Guarinite | $(Ca, Na)_3(Fe, Mn, Zr, Cb)(SiO_4)_2(O, F, OH)$ |
| Johnstrupite | $(Ca, Na, Ce)_3(Al, Mg, Ti, Ce)(SiO_4)_2(F, OH)$ |
| Rinkite | $(Ca, Na)_{15}(Ce, Zr, Ti)_7(SiO_4)_{10}F_7$ |
| Rinkolite | $(Ca, Na)_6(Ce, Ti)_3(SiO_4)_4(F, OH)_4$ |
| Mosandrite | $(Ca, Na)_{12}Ce_3(Zr, Ti, Mg)_4(SiO_4)_{10}F_5$ |
| Låvenite | $(Ca, Na)(Zr, Cb, Fe, Ti, Mn)(SiO_4)F$ |
| Britholite | $Ca_3Ce_4[(Si, P)O_4]_4(OH, F)_3$ |
| Hellandite | $Ca_3(Y, Er)_4(Al, Fe''', Mn''')_5(SiO_4)_6(OH)_9$ |
| Lessingite | $Ca_4(Ce, Y, Er, La)_7(SiO_4)_6(OH, F)_5$ |
| DATOLITE FAMILY: | |
| Datolite | $Ca_2B_2(SiO_4)_2(OH)_2$ |

| | |
|---|---|
| Euclase | $Be_2Al_2(SiO_4)_2(OH)_2$ |
| Homilite | $Ca_2Fe''B_2(SiO_4)_2O_2$ |
| Gadolinite | $Y_2Fe''Be_2(SiO_4)_2O_2$ |

*Miscellaneous orthosilicates:*

| | |
|---|---|
| Topaz | $Al_2SiO_4(F, OH)_2$ |
| Axinite | $H(Ca, Mn, Fe)_3Al_2B(SiO_4)_4$ |
| Ilvaite | $Ca(Fe, Mn)_2Fe'''(SiO_4)_2(OH)$ |
| Tinzenite | $Ca_2Al_2Mn'''(SiO_4)_4$ |
| Eulytite | $Bi_4(SiO_4)_3$ |
| Zunyite | $Al_8(SiO_4)_3(F, Cl, OH)_{12}$ |

## Subsilicates:

### ALUMINUM SUBSILICATE FAMILY:

| | |
|---|---|
| Andalusite | $Al_2SiO_5$ |
| Sillimanite | $Al_2SiO_5$ |
| Mullite | $Al_6Si_2O_{13}$ |
| Kyanite | $Al_2SiO_5$ |
| Staurolite | $Fe''Al_4Si_2O_{10}(OH)_2$ |

*Kentrolite group:*

| | |
|---|---|
| Kentrolite | $Pb_3Mn_4'''Si_3O_{15}$ |
| Melanotekite | $Pb_3Fe_4'''Si_3O_{15}$ |

| | |
|---|---|
| Beckelite | $Ca_3(Ce, La, Di)_4Si_3O_{15}$ |

*Titanium subsilicates:*

| | |
|---|---|
| Titanite | $CaTiSiO_5$ |
| Lorenzenite | $Na_2(Zr, Ti)_2Si_2O_9$ |
| Ramsayite | $Na_2Ti_2Si_2O_9$ |
| Fersmanite | $Ca_4Na_2Ti_4Si_3O_{18}F_2$ |
| Molengraafite | $Ca_4Na_4(Mg, Fe'')AlTi_4Si_6O_{28}(OH)$ |
| Lamprophyllite | $Ca_2Na_6Ti_6Si_6O_{28}(OH, F)_2$ |

*Miscellaneous subsilicates:*

| | |
|---|---|
| Dumortierite | $AlB_8Si_3O_{19}(OH)$ |
| Serendibite | $Ca_2Mg_4Al_6B_2Si_4O_{26}$ |
| Ardennite | $(Ca, Mn, Mg)_4Al_4(As, V)Si_4O_{18}(OH)_5$ |
| Sapphirine | $Mg_5Al_{12}Si_2O_{27}$ |
| Kornerupine | $MgAl_2SiO_6$ |
| Cappelenite | $Ba(Y, Ce, La)_6B_6Si_3O_{24}(OH)_2$ |
| Melanocerite | $Ca_{16}Na_4(Y, La)_3(Zr, Ce)_6B_3Si_{12}O_{57}F_{12}$ |
| Mackintoshite | $(U, Ce, Th, La, Y, Pb)_2SiO_5$ |

### URANIUM SILICATES:

*Uranophane group:*

| | |
|---|---|
| Uranophane | $CaU_2Si_2O_{11} \cdot 7H_2O$ |
| Sklowdowskite | $MgU_2Si_2O_{11} \cdot 7H_2O$ |

| | |
|---|---|
| Kasolite | $Pb_2U_2Si_2O_{12} \cdot H_2O$ |
| Soddyite | $U_5Si_2O_{19} \cdot 6H_2O$ |

## III. DISCUSSION OF THE CLASSIFICATION

The writer is aware of the probability that a considerable number of minerals will be found, when more structural data are available, to have been misplaced in the classification. However, the general outline of the classification and the positions of the most important groups will probably stand as given. The chief uncertainties in the classification arise from insufficient data on rare minerals, many of which offer almost insurmountable difficulties in structural studies. The structures of these are not likely to be solved soon. In the meantime, the writer believes, the results of a new technique, and a newer and more adequate theory should be applied to the study of the silicates and to their classification. One must first have a classification in order that it may be modified and further improved. Further, an attempt to make the classification of all the silicates gives direction to future study since exceptions and modifications of the theory appear in the course of a systematic examination of the data.

The classification proceeds, in general, from the most siliceous types to those having the least amount of silica, namely the orthosilicates. At the end of the classification certain titano-silicates and boro-silicates are introduced. It is difficult to decide which of the low-silica compounds are no longer essentially silicates. The point of view here taken is that a mineral ceases to be a silicate when the $SiO_4$ tetrahedra are no longer the dominant motif in the structure. The classification, therefore, can have no sharp break at the end; it would naturally fit onto a similar grouping of titano-silicates and boro-silicates and some other rare, low-silica-content minerals.

### Silica Type

The minerals of this type, except the crystalline forms of silica, are composed almost exclusively of alkali or calcium aluminum silicates, the composition being such that $2(Al+Si)=O$. Apparently only a few exceptions to this composition are of this type, namely, danalite, helvite and cordierite. Another noteworthy feature of this type is the presence, in some of its groups, of such unusual components as Cl, S, $SO_4$ and $CO_3$. These are apparently held in the large spaces of the open network, which is characteristic of this structural type. It is to be noted that the structure of these minerals is analogous to that of the crystalline forms of silica, which are also three-dimensional networks of $SiO_4$ tetrahedra. These silicate structures differ from silica in that some of the tetrahedra in the cell are $AlO_4$. As a consequence of this, other atoms, usually the large alkali or alkaline earth atoms also enter into the structure, in order to balance the valence bonds of the oxygens. It is for this reason that the total valences of the alkali or calcium atoms are always equal to the number of aluminum atoms in the general formula.

Since the three-dimensional network is the so-called open structure, the density of this type of silicate is lower than that of any other type, the range being from 2 to 3, with most of the members occupying an intermediate position. It is likewise true that the mean refractive index is also low for these silicates. Further, because of the nature of the three-dimensional network, the tendency of producing equidimensional crystals is shown in the type. Since the chemical and physical properties of this type are so distinctive, no particular difficulty is encountered in recognizing its members.

*Silica group:* $SiO_2$. The classification of the silicates properly begins with the crystalline forms of silica because these substances show in their structures the same silicon-oxygen tetrahedra as are found in the silicates. Further, in all the forms of silica which have thus far been studied (four out of the seven crystalline modifications) the tetrahedra are linked together in such a way as to share corners with four other tetrahedra to produce the three-dimensional network, which is the linkage of our first type.

Since the silica minerals show no appreciable variation from pure $SiO_2$, for the sake of brevity no discussion of other aspects of these minerals is attempted here.

*Petalite group:* $W\ Z_5O_{10}$. Petalite $(Li, Na)AlSi_4O_{10}$. The mineral is essentially a lithium compound. The only considerable substituting atom is Na. The range of the ratio Li:Na is from 15:1 to 2.3:1 (Dana 1892, p. 312, anal. 4).

Milarite $6(Ca, K)(Al, Be, Si)_5O_{10}$ with $Ca:K=2:1$ and $Al:Be:Si=1:2:12$, the expanded form being: $Ca_4K_2Be_4Al_2Si_{24}O_{60}$ with a small amount of water possibly belonging in the formula. This is one of the few silicates in which the Be apparently plays the same role as Si in the structure. Incidentally it is only very recently that this old species was found to contain Be (Palache 1931).

Leifite $Na_4Al_2Si_9O_{22}F_2$. Because of its general physical characteristics and composition this little known mineral is placed here. It is perhaps more closely related to the members of this group than any other.

*Feldspar group:* $W\ Z_4O_8$, with $W=Na, Ca, K, Ba$ and to some extent $Na_2$, and $Z=Si-Al$; $Si:Al=3:1$ to $1:1$. Since all feldspars contain a certain minimum amount of Al and Si the general formula may be somewhat more specifically stated as

$$W\ Al(Al, Si)Si_2O_8$$

with only one atom out of the four Al+Si atoms participating in the Al, Si substitution found in some members of the feldspar series. The usual division into monoclinic and triclinic members is here made and the two symmetry types in the feldspars are retained because no new evidence to show that orthoclase is triclinic has been presented, and further evidence of some value (Taylor 1933) has shown that it is probably monoclinic.

The problem of miscibility in the monoclinic feldspars is rather complicated by the wide range of temperature of formation. It can be laid down as a general rule, in the feldspars as well as in other silicates, that a higher temperature of formation allows greater miscibility of the components. Thus K, Na, Ba may be, and very likely are, completely miscible at high temperatures of formation. The ordinary temperatures at which we study the minerals show miscibility ranges which are very different. It is because of this difference in miscibility that we have the so-called exsolution phenomena. Unmixing is probably a rather sluggish process in the feldspars so that we might expect certain members formed at high temperatures to exhibit greater miscibility than the same minerals formed at lower temperatures.

In the orthoclase series, K and Na are probably not miscible to any considerable extent at low temperatures of formation, as in low-grade metamorphism and in most vein deposits. However, analyses of higher temperature orthoclases indicate as much as 40 per cent Na may replace K (Alling 1921).

Barbierite, the supposed monoclinic soda-feldspar has not been shown to exist as such. The fact that Na replaces some K in orthoclase does not, of course, necessitate the supposition that a pure monoclinic sodium member exists. This fallacy is another example of the dangers of postulating so-called "end members."

Apparently a more or less complete series of the K, Ba monclinic feldspars is known. The mineral hyalophane has the composition (K, Ba)-Al(Al, Si)$Si_2O_8$ with K:Ba in all proportions. However, some evidence (Taylor Darbyshire and Strunz 1934) indicates that celsian, the pure Ba feldspar, may be triclinic. If this is true, the K, Ba series may be strictly two overlapping series having physical properties sufficiently alike so that we cannot detect the break.

The triclinic feldspars are divided into two main series: the microclines, and the plagioclases.

The microclines, with the formula (K, Na)$AlSi_3O_8$ are generally homogeneous, even with considerable amounts of Na. Anorthoclase is often, however, not homogeneous, and as such cannot be considered as a definite mineral compound. In other words, Na does not enter into the composition of the microcline members to any large extent. This fact may be an expression of the lower temperature range of formation of the microclines as compared with the orthoclases, and a consequent lessening of the miscibility of Na and K. In albite, $NaAlSi_3O_8$, we have only a moderate amount of K (15 per cent) as a maximum, so that we probably have no overlapping series from both ends.

The plagioclases are seemingly a straightforward, single isomorphous series with examples known throughout the range between albite and anorthite. Recent $x$-ray work (Taylor, Darbyshire and Strunz 1934) has shown, however, that the anorthite cell is double the albite cell and that the change occurs somewhere about $Ab_1$ $An_1$. This evidence seems to indicate that with respect to the $x$-ray properties there are really two series, an albite-labradorite portion, and a labradorite-anorthite part. Yet none of the other physical measurements in the plagioclases indicates that such a break occurs, so that one may infer from this that even though we have two series, they are so close in their physical properties that we do not find any measurable differences. When two such series are so closely related, for our purposes we may consider them as one.

Anemousite, the feldspar containing the so-called carnegeite molecule $Na_2Al_2Si_2O_8$, a supposed isomer of nepheline, has a composition which may be expressed as $(Ca, Na, Na_2)Al(Al, Si)Si_2O_8$; that is to say, some of the Ca is replaced in the structure by $Na_2$. This is possible in the open network in which spaces are available to accommodate an extra atom, but it is a rarity in the silicates as a whole. The carnegeite molecule is not a feldspar and we do not, therefore, include it in our list. Only a small amount of $Na_2$ has been found to enter into the feldspar composition.

Pollucite $(Cs, Na)_4Al_4Si_9O_{26} \cdot H_2O$ with $Cs:Na = 4:1$ somewhat variable. There are two formula weights of the above in the unit cell as determined by the writer ($a_0 = 13.66$ Å) and checked by recent work of Strunz (1936).

The formula is derived from the analyses in Dana (1892, p. 344) and the work by Wells (1891). It is perhaps stretching relations to group this mineral with leucite as is commonly done in textbooks. Presumably the fact that both are isometric is the only reason for grouping them together.

Leucite $WZ_3$ $O_6$, or more specifically $KAlSi_2O_6$; Na, Ca usually less than 1 per cent and Li, Rb, Cs in traces. Leucite is, as minerals go, a fairly pure specific compound with little variation in its composition. The zeolite analcite $NaAlSi_2O_6 \cdot H_2O$ is possibly closely related in structure, but no evidence is found of an isomorphous relationship between the two.

*Nephelite group:* $WZ_2O_4$. Nephelite $(Na, K)(Al, Si)_2O_4$, sometimes with Ca and Mg in very small amounts; $Na:K = 35:1$ to $3:1$; $Si:Al = 1.1:1$

rather uniformly. Bannister (1931) has shown that the unit cell contains 32 oxygen atoms so that the composition of the unit cell is eight times our formula.

One of the remarkable features about the chemistry of nephelite is the uniform failure of Al:Si ratio to be unity. There is nearly always a slight preponderance of Si so that the ratio is, as given above, 1.1:1. Corresponding with this slight deviation in the ratio of Si:Al in the natural nephelites, we have a decrease in the (Na+K) atoms so that the formula is only approximately true. For a detailed account of the chemical and physical characteristics of the nephelites reference should be made to Bannister's excellent work (1931).

Kaliophilite $WZ_2O_4$, with W=K predominantly, and Na subordinate; the ratio K:Na=53:1 to 4:1; a trace of Ca in most cases; Z=Si:Al =1:1. The unit cell probably contains 54 units of the above formula (Bannister 1931). The writer is inclined to agree with Bannister in his statement that a continuous isomorphous series (Bowen 1917) between kaliophilite and nephelite has not been definitely shown to exist in nature.

Eucryptite $WZ_2\,O_4$, with W=Li; Z=Si−Al; Si:Al=1:1.

*Cancrinite group:* $W_{7-8}Z_{12}O_{24}\cdot N\cdot sH_2O$; W=Na, Ca, K with Na and Ca predominating; Z=Si:Al=1:1.

Cancrinite, which is here meant to include all of the minerals of the group except those containing Cl, is rather variable in composition within the limits indicated by the group formula. Since no study of the analyses has appeared in the form taken here, a résumé is given in the following table.

TABLE 3. CANCRINITE: ANALYSES (BÖRGSTROM 1930)

| | Na | K | Ca | Al | Si | O | $CO_3$ | $SO_4$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Synthetic Friedel | 7.17 | .50 | | 6.02 | 5.98 | 23.79 | 1.05 | | 2.30 |
| Brevig yellow | 6.77 | .07 | .55 | 5.40 | 6.60 | 23.99 | 1.29 | | 2.96 |
| Litchfield | 6.38 | .02 | .93 | 5.90 | 6.10 | 23.69 | 1.51 | | 2.16 |
| Litchfield | 6.66 | .06 | .97 | 6.06 | 5.94 | 23.98 | 1.32 | | 2.99 |
| Miask | 5.86 | .04 | 1.09 | 5.92 | 6.08 | 23.63 | 1.47 | | 2.96 |
| Brevig Rose | 6.23 | .05 | 1.29 | 5.80 | 6.20 | 24.02 | 1.51 | | 2.52 |
| French River | 5.10 | .18 | 1.46 | 6.02 | 5.98 | 23.71 | 1.39 | | 2.10 |
| Colo. | 5.19 | .11 | 1.61 | 6.14 | 5.86 | 23.59 | 1.61 | | 2.68 |
| Beaver Creek | 6.31 | .32 | .79 | 6.08 | 5.92 | 23.73 | .76 | .61 | 2.91 |

From this table of atomic ratios, on the basis of Al+Si=12, the compositional ranges may be stated as:

(a) $Na_8Al_6Si_6O_{24}\cdot CO_3\cdot 2H_2O$
(b) $(Na, K)_6CaAl_6Si_6O_{24}\cdot CO_3\cdot 2\text{–}3H_2O$
(c) $(Na, K)_6Ca_2Al_6Si_6O_{24}\cdot 2CO_3\cdot 2\text{–}3H_2O$

The compositions of the most reliable analyses indicate a tendency for Ca to increase as Na+K decreases, and also for $CO_3$ to increase with the Ca. Water seems to bear no exact relation to the other constituents, varying from 2 to 3 per 24 oxygen atoms. The Al:Si ratio is fairly uniformly 1:1.

Table 4. Microsommite and Davyne

| | Na | K | Ca | Al | Si | O | $CO_3$ | $SO_4$ | Cl |
|---|---|---|---|---|---|---|---|---|---|
| Microsommite Vesuvius v. Rath | 3.00 | 2.62 | 2.15 | 6.11 | 5.89 | 24.31 | | .22 | 2.76 |
| Microsommite Vesuvius Scacci | 3.23 | 1.80 | 2.09 | 6.42 | 5.58 | 23.44 | | .76 | 2.36 |
| Davyne Mt. Somma | 3.93 | 1.66 | 2.02 | 6.14 | 5.86 | 23.78 | .36 | .53 | 2.16 |

Microsommite and Davyne $W_8Z_{12}O_{24}(Cl, SO_4, CO_3)_3$; W=Na, Ca, K; Z=Al+Si; Al:Si=1:1. $(Na, K)_6Ca_2Al_6Si_6O_{24}\cdot Cl_2\cdot CO_3$ is the most common composition, but Na+K, with Na dominant, may vary from 5 to 6 with a consequent variation in the $Cl:CO_3$ ratio (Table 4). The chief differences between this series and the cancrinites are that in the former there are considerable quantities of Cl and some $SO_4$, and that much more K is present; water is absent.

*Sodalite group: Sodalite series:* $W_{7-8}Z_{12}O_{24}N_{1-2}$; W=Na predominantly, Ca common; Z=Si:Al=1:1; N=Cl, S, $SO_4$, $CO_3$ rarely. This group might be said to be the isometric equivalent of the cancrinite group, with some modifications, as appears in the formulae in the classification.

There is no direct evidence that the compound $Ca_4Al_6Si_6O_{24}\cdot SO_4$ is a true member of this series. The analyses quoted (Barth 1932) do not support the contention, and Barth's general formula is here not used for that reason. Jaeger (1929) has shown that the artificial aquamarines have a composition which may be referred to our general formula.

*Danalite series:* $X_8Z_{12}O_{24}\cdot S_2$; X=Mn, Fe, Zn; Z=Si+Be; Si:Be=1:1; or $(Mn, Fe, Zn)_8Be_6Si_6O_{24}\cdot S_2$. It is to be noted that the two species of this series (danalite with Zn, helvite without) are closely related to the sodalites. However, the elements (Mn, Fe″, Zn) are rarely found in this type of silicate; and further, Be apparently substitutes for Si in the tetrahedral network. The unit cell dimensions of danalite and sodalite are closely similar (Barth 1926).

*Scapolite series:* $W_4Z_{12}O_{24}N$; W=Ca, Na; K to $4\frac{1}{2}$ per cent; Z=Si+Al, Si:Al=3:1 to 1:1; N=Cl, $CO_3$; $SO_4$ subordinate, (OH) rare. Intermediate members are mizzonite, dipyre, and wernerite. These are members of a series of which marialite and meionite are the end components; neither of these two are, however, pure compounds as found in nature. In marialite $Na:Ca<4:1$ and in meionite $Ca:Na<8:1$. Most of the members of the series are higher in Ca than in Na+K. Incidentally it may be worth noting here that one of Barth's (1932) end components of the sodalite group is close in composition to the calcic end of the scapolite series. Presumably under the temperature conditions prevailing, the tetragonal form of calcium aluminum silicate is stable rather than the isometric form, sodalite.

The chief chemical differences of this series as contrasted with the preceding two groups are (1) the variability of the Si:Al ratio, as in the feldspars; (2) the lower Ca+Na molecular percentage. Structurally they are related in that they are made up of three dimensional networks of Si and Al tetrahedra.

*Zeolite family:* $W_mZ_rO_{2r}\cdot sH_2O$; W = Na, Ca, K, Ba, Sr; also rarely Mg, Mn; Z = Si+Al; $Si:Al>1$; $s$ variable. A more specific and rather more complex statement of the composition of the zeolites is:

$$(Na, K)_m(Ca, Ba, Sr)_nAl_{2n+m}Si_rO_{2(2n+m+r)}\cdot sH_2O.$$

The zeolites have been the subject of investigation and theory since the earliest days of mineralogy because of the large number of species within a limited range of composition. Many studies have been made attempting to show the constitutional relations between the members of this family. Tschermak's classical work remains as the best example of the studies according to the older theories. Winchell (1925) has contributed a series of papers embodying some of the newer concepts. Bannister and Hey have made careful chemical and $x$-ray studies of many of the zeolites, which they have described in a series of nine splendid papers over a period of six years. The ideas presented below are to a large extent a digest of those expressed in the works above mentioned, with some modifications and additions, as indicated.

The zeolites, as well as the other members of this silicate type, have certain chemical characteristics, as expressed in the formula previously given.

The earliest noted relation (Tschermak 1917; 1918) was that indicated in the part of the formula having to do with the alkalies, calcium, and aluminum: $(Na, K)_m(Ca, Ba, Sr)_nAl_{2n+m}$. The number of Al atoms in the formula is equal to the combined valences of the univalent and bivalent elements.

The second important feature, first thoroughly investigated by Winchell (1925), had to do with the relation $Al_{2n+m}Si_rO_{2(n+m+r)}$ that is, the sum of Al+Si is equal to half the number of oxygen atoms in the formula. This, it will be noted, is the fundamental chemical characteristic of all the members of this silicate type, and it is our reason for placing the zeolites in this part of the classification. The two chemical characteristics above referred to are really fundamentally the same since the first relation follows from the second.

The writer in his investigations of zeolite compositions has found no instance where the ratio Al:Si is greater than 1; Al does not exceed Si in the formula. It is for this reason that some of the Winchell "end members" are not accepted here.

There is a definitely limited range of miscibility in the zeolites, so that the compositional range of a series is narrow. This probably means a narrow range of stability for most zeolites, and it may explain the large number of species in the family.

Most of the isomorphous substitutions are, as Winchell (1925) has shown, atom for atom, but there are undoubtedly cases where $Na_2$ (and perhaps $K_2$) replaces Ca. Hey (1930) has noted this same deviation from the usual silicate atom-for-atom replacement, and explains it as a replacement subsequent to the formation of the crystal, that is, a method analogous to the method of artificial base exchange in the zeolites.

Water seems to occupy definite positions in the crystal lattice of the zeolites (Taylor 1930), but because of the open structure of the network it is easily driven off giving a continuous dehydration curve in most cases. The framework of the structure is often preserved even after the water is driven off. For a detailed account of dehydration and rehydration see Hey (1930; 1935).

There are a few well-defined groups in the zeolites. These have long been recognized. On the whole, few series are known; and even where the compositions and crystal forms are close together, as in the natrolite group, we have little isomorphism. For the most part the formulae presented in the classification are rather complex. Recent $x$-ray work (Bannister) and Hey's careful study, as well as Winchell's papers agree that complex formulae are needed to express adequately the composition. The classification gives the zeolite formulae which, in the writer's opinion, express the composition and agree with recent chemical and $x$-ray work. A number of the species listed are not yet well defined. The precise relationships in all the groups are not well established. However, the general features as outlined in the classification are, it is believed, approximately correct.

*Mordenite series:* With Ca:Na:K=6:1:3 to 3:6:1; From the variations given it is evident that mordenite forms a rather extensive series between Ca, Na, and K members, with the K members subordinate. The formulae by Schaller (1932) are less complex. Hey (1934) has pointed out that the $x$-ray photographs of mordenite and ptilolite are identical.

At any rate, the composition of ptilolite fits into the mordenite series and it is here considered as a member of that series.

The minerals of the heulandite group are apparently closely related crystallographically as well as chemically. The last three may form a series, but no direct evidence of this is available since the crystal data of the three species are not so closely similar as that usually associated with a serial relationship (Tschermak 1917 and Winchell 1925). Clinoptilolite, while it has a composition much like mordenite has been shown to be structurally identical with heulandite (Hey and Bannister 1934). Mordenite and heulandite have certain crystallographic and chemical similarities and they are probably related structurally; the former is essentially the Na mineral and the latter the mineral with dominant Ca

*Stilbite group:* This group is not particularly well defined. Certain crystallographic similarities have been noted by Tschermak (1917) and others, between the first five minerals listed here. Stilbite, epidesmine and harmotome are, in addition, obviously related chemically, as shown in the classification. Phillipsite, and the rare wellsite, are definitely related crystallographically to harmotome and stilbite, yet the compositions are widely different. This group probably consists of two main series which are isostructural but not isomorphous. This would mean structurally that some of the positions which are vacant in the stilbite structure are perhaps occupied by Ca or Na in the phillipsite structure.

The last three minerals listed under the stilbite group are related in composition to the other members of the group. Crystallographic similarities have been noted (Tschermak). Stellerite and erionite are rare species and have not been fully invesitgated. Tschermak lists erionite with stilbite, and stellerite has been shown to be very close to stilbite in its crystallographic properties.

*Chabazite group:* The first two minerals of this group are closely related in crystallographic properties. However, the compositions, as shown in the classification, are very different. The two minerals, as Winchell (1925) points out, are certainly not members of an isomorphous series. They are probably isostructural, with $Na_2$ of gmelinite occupying positions, half of which are occupied by Ca in chabazite. The probable isostructural relations can be shown by writing the formulae as follows:

| | |
|---|---|
| Gmelinite | $Ca_2(Na_2)_5Al_{14}Si_{26}O_{80}\cdot 40H_2O$ |
| Chabazite | $Ca_7Al_{14}Si_{26}O_{80}\cdot 40H_2O$ |

*Thomsonite group:* The members of this group probably do not form a series. There are some variations in the composition of thomsonite, as indicated in the formula, but the other members of the group are comparatively rare, and no variation has been shown to exist. The chemical compositions of gonnardite and arduinite indicate that the two species are probably identical. Optical and other physical data are lacking, in part, for these two species, so that further work must be done to establish their relation. Ashcroftine is the so-called kalithomsonite of Gordon (1924). Hey and Bannister (1933) have shown that this supposedly K-rich thomsonite is not really a member of the thomsonite series, but differs in having a very much larger unit cell (nine times) and truly tetragonal symmetry. Thomsonite and gonnardite are probably isostructural since their cell dimensions are similar (Hey and Bannister) as well as their compositions.

*Natrolite group:* The minerals of this group are closely related structurally as shown by the remarkable similarity of their *x*-ray diffraction patterns (Hey and Bannister 1933). The unit cells are, however, multiples of each other, and in detail the *x*-ray pictures differ somewhat, so that the minerals here placed in the group are not really members of a series, but are isostructural.

Natrolite has 80 oxygen atoms in the unit cell. Of the 16 Na atoms usually contained in the unit, one is sometimes K, thus Na:K=15:1. There is also some substitution of Ca for $Na_2$ but only to a maximum of $Na_4$. The Al:Si ratio is essentially constant (Hey, with Bannister, 1932.)

Mesolite has a cell three times the volume of that of natrolite. Consequently the number of oxygen atoms is 240. The formula given represents $\frac{1}{8}$ of the unit cell contents. Few silicates are known with such huge unit cells. In fact, the zeolites in general have large units in comparison with most other silicates. Edingtonite is rather an exception among zeolites in having an average-sized unit cell, containing but 20 oxygen atoms, beside those in the $H_2O$.

*Miscellaneous zeolites:* The minerals listed are not in any sense a group; they are merely those zeolites which have no well-defined position in any of the previously discussed groups. Faujasite has been analysed but twice and its composition is not certain. Analcite is a well-established species with a fairly definite composition; only small amounts of Ca and K enter into the composition.

Laumontite shows some variation in composition from an almost pure Ca member to a member with the ratio Ca:Na=5:2. It is to be noted here that laumontite has a composition almost identical with that of chabazite, except that the latter has more water.

Ferrierite $Mg_2Na_4Al_8Si_{32}O_{80}\cdot 20H_2O$? This mineral has an uncertain composition. It is unique among zeolites in carrying important amounts of Mg; as far as known it shows no definite relationship to any other zeolite in its physical and crystallographic properties.

Laubanite $Ca_2Al_2Si_5O_{15} \cdot 6H_2O$ is apparently a zeolite; but its composition, as given, does not conform with the general zeolite formula and is open to doubt. The writer has examined a specimen of this material from the type locality and finds that it is made up of an aggregate of at least two minerals. The study was carried no further, since the inhomogeneous material was finely intermixed and little hope was entertained of separating the individual constituents.

Didymolite, given as $Ca_2Al_6Si_8O_{27}$, has no water in the analysis (Ford, 1915). However, the optical properties as reported (Larsen and Berman 1934) cannot possibly be in agreement with this composition, since any calcium aluminum silicate would certainly have a mean index greater than 1.50. This substance, if its optics are correct, is probably a zeolite and the water has been overlooked.

Dachiardite has a doubtful composition, as given, since it is undoubtedly a zeolite and yet the relation between Na+Ca and Al is not in agreement with the general zeolite formula-relations. A new analysis of this interesting zeolite is desirable but little material is available.

Cordierite $(Mg, Fe, Mn)_2(Al, Fe)_4Si_5O_{18} \cdot H_2O$. This mineral is apparently of the silica type. However, the presence of (Mg, Fe, Mn) is unusual in this type, and it is with some uncertainty that the writer places it here in the classification. With its low refractive index and low density, the mineral fits into this type; but until structural details are available, the classification of this mineral is uncertain.

## DISILICATE TYPE

This important silicate type has the following chief chemical characteristics:

The ratio of $Z:O=2:5$, where Z is predominantly Si, but in most of the families Al, with the co-ordination number 4, is a prominent element of the Z kind. The ratio Si:Al is greater than 1:1, with some important exceptions in the brittle micas. Since most of the members of this type are hexagonal or pseudo-hexagonal, in conformity with the pattern of the two-dimension network (Fig. 2), the smallest unit of the structure yields a composition $Z_4O_{10}$ for the pseudo-hexagonal unit or $Z_6O_{15}$ for the truly hexagonal units.

Another chemical characteristic of the type is the presence, in nearly all members, of hydroxyl or the equivalent fluorine. In friedelite Cl apparently plays the same role as the (OH) and F.

In many of the chloritic minerals, in addition to (OH) some $H_2O$ is also found, thus there are two kinds of water in the composition. This dual role of water gives rise to the characteristic dehydration curves of the chlorites (Orcel 1927). The (OH) is more firmly held in the structure and consequently is driven off at a higher temperature as compared with the more loosely held $H_2O$.

*Physical properties of the disilicate type:* The minerals of this type are particularly noteworthy in having a micaceous cleavage which is the most perfect cleavage known in crystals, with the possible exception of graphite. This cleavage is always taken as the basal plane {001}. It is assumed, and has been proved in many instances, that this cleavage plane represents the plane of the two-dimensional network which is the fundamental structural feature of the type (Fig. 2). Since this network as previously stated, is hexagonal in its pattern, the dominant habit in this type is a hexagonal plate, as exemplified in the micas, the chlorites, and the crystalline members of the kaolin group.

On the whole, the type is made up of minerals with medium hardness, but some members high in water content are soft. The Al-silicates are also softer than other members of the type. An interesting optical feature of these minerals is that the negative acute bisectrix is almost always normal, or nearly so, to the cleavage face. Ottrelite, chloritoid and some of the chlorites are exceptions to this rule. Wooster (1931) has discussed the structural basis of this optical behavior in platy substances.

A few platy silicates belong to the Pyrosilicate type.

*Aluminum disilicates:* $Y_p(Si_4O_{10})(OH)_{3p-4} \cdot sH_2O$; $Y = Al$, $Fe'''$ subordinate, Cr rare; $p = 2$ to 4; $s = 0$ to 4. The aluminum silicate family is made up for the most part of rather finely crystalline species, whose fineness often borders on the submicroscopic. Some of the minerals in this family are so finely crystalline that they have been thought to be amorphous. However, *x*-ray powder pictures have shown these to be crystalline. A few Al silicates are probably truly amorphous. This may account for the considerable variability in composition as reported (Tomkeieff 1933).

The kaolins are made up of several members, all with the same composition. Halloysite has the kaolin formula plus $H_2O$. Volchonskite has $Y = Al$, $Fe'''$, Cr.

Canbyite and batchelorite are close to the kaolins with some extra water. Chloropal is presumably an amorphous equivalent of batchelorite with $Fe'''$ instead of Al.

Close to beidellite $Al_8(Si_4O_{10})_3(OH)_{12} \cdot 12H_2O$ is montmorillonite whose formula may be written as $(Al, Mg)_8(Si_4O_{10})_3(OH)_{10} \cdot 12H_2O$ with $Al:Mg = 6:2$, namely as a beidellite with part of the Al replaced by Mg. Nontronite is a member of the beidellite group (Gruner 1935). He writes these formulae somewhat differently.

Apparently little isomorphism exists in these minerals. The finely divided aluminum silicates do show a variation in composition but the variability is not due to the formation of mixed crystals, but rather to a probable adsorption of water and gelatinous silica.

Talc shows little variation in composition from that given above. A small amount of Fe and Ni is often present, also Al in inappreciable amounts.

*Antigorite series:* The mineral antigorite is apparently a dimorphous form of serpentine which is distinctly fibrous and of the metasilicate type. Since the composition of this mineral corresponds to an aluminum-free chlorite (Tschermak 1890), it is currently considered as an "end member" of the chlorite series. The writer is not inclined so to consider antigorite, since a definite composition seems to be associated with the mineral. No continuous series has been shown to exist between antigorite and chlorite. As will be shown later, a certain minimum of $Al+Fe'''$ is always present in the chlorites; and it is, therefore, the writer's opinion, supported by a recent work by Selfridge (1936), that antigorite is not a chlorite.

Connarite is more hydrous than the other members of the group. Little is known of variations in its composition since so few analyses have been made.

The members of the *Freidelite group* are all rare minerals on which the data are not plentiful. However, in their physical properties they are undoubtedly closely related. They have all the characteristics of the typical platy silicates, including the micaceous cleavage. They are different from most platy silicates in that they are probably hexagonal or rhombohedral. Most other silicates of this type are pseudo-hexagonal, and really monoclinic or orthorhombic. The difference is expressed chemically in the $Si_6O_{15}$ composition, since a hexagonal cell would probably have as its unit 6 silicons rather than the customary 4 of the other platy silicates.

Friedelite, it is to be noted, has some Cl in its composition, and apparently this element substitutes for (OH) in part. Some arsenic has been noted in this unusual mineral so that it probably forms a series with schallerite (Palache 1935). Fe is also reported in small amounts; a higher percentage of Fe enters into the isomorphously related pyrosmalite. We probably have a series varying to schallerite and to pyrosmalite. Ferroschallerite is a recently described equivalent of schallerite with Fe and Zn in considerable amounts (Bauer and Berman 1930).

Zeophyllite is apparently a Ca equivalent of friedelite, but no intermediate compounds are known and it is doubtful if a series could form. The only rhombohedral form found on zeophyllite corresponds in angle ($\rho=78°$) to the prominent form $t\{0.15\cdot\overline{15}.2\}$ of friedelite. This mineral has heretofore been referred to the zeolites with which it has little in common, in the writer's opinion.

Centrallasite and truscottite from their compositions and physical properties are obviously closely reated. The writer is inclined to consider the two as varying only in the content of Mg. In truscottite Ca:Mg =4:1; centrallasite is the Ca end component of the series (Larsen and Berman 1934, p. 158). Gyrolite is probably identical with centrallasite, although the water content is given as being different. A comparison of the optical properties of the two shows their essential identity.

*Miscellaneous non-aluminum disilicates.* The first two of the minerals listed in the classification are comparatively rare. Bementite has not been observed in crystals, but it is definitely a platy silicate. The negative acute bisectrix emerges on the best cleavage; the other cleavages noted for this mineral are districtly inferior to this perfect cleavage.

Errite is a rare species, recently described (Jakob 1923). A closely related, and perhaps identical, mineral, parsettensite was described at the same time. These two are micaceous in habit and conform with the general physical criteria of this type.

Apophyllite is often placed with the zeolites for several reasons. It is nearly always associated with zeolites and it has a considerable amount of water. However, no other mineral placed in the zeolite family lacks Al, and an *x*-ray structural study (Taylor and Naray-Szabo 1931) has shown that this mineral is of the platy silicate type.

*Anhydrous non-aluminum disilicates:* Gillespite and sanbornite, two rare minerals, occur together and have recently been so described (Rogers 1932). The exceedingly good micaceous cleavage and general optical properties, as well as the simple chemistry, are unmistakable evidence that these these minerals are properly placed here.

*The chlorite family:* $X_nZ_4O_{10}(OH)_{2(n-2)} \cdot sH_2O$. Pauling (1930 B) deduced a similar formula from structural considerations of the chlorite-like minerals. It is an important characteristic of the minerals of this family that Al and some Fe''' enter into both the X and Z parts of the above formula in equal amounts. Tschermak (1890; 1891) and later Winchell (1926) demonstrated this fact in another way. The general formula may be more specifically written:

$$(\mathrm{Mg, Fe''})_{n-p}(\mathrm{Al, Fe'''})_{2p}\mathrm{Si}_{4-p}\mathrm{O}_{10}(\mathrm{OH})_{2(n-2)} \cdot s\mathrm{H_2O}$$

where the $(\mathrm{Al, Fe'''})_{2p}$ is in part united with (Mg, Fe) and in part with the Si so that the resultant formula is, as given at the beginning of this section

$$[(\mathrm{Mg, Fe})_{n-p}(\mathrm{Al, Fe'''})_p][(\mathrm{Al, Fe'''})_p\mathrm{Si}_{4-p}]\mathrm{O}_{10}(\mathrm{OH})_{2(n-2)} \cdot s\mathrm{H_2O}$$

or

$$(\mathrm{Mg, Fe'', Al, Fe'''})_n(\mathrm{Al, Fe''', Si})_4\mathrm{O}_{10}(\mathrm{OH})_{2(n-2)} \cdot s\mathrm{H_2O}.$$

Variations in the number *n* give rise to the different groups of the family. The different $p$ values are, in general, responsible for the serial variations. The vermiculites differ from other groups of the family principally in having a higher $s$ value. As will be shown, the terms $n$, $p$, and $s$, and the ratios $Mg/Fe''$, $Al/Fe'''$ completely define any species of this family. Since the members of the family are so closely related chemically, it becomes a somewhat arbitrary procedure to divide them into groups on the basis of $n$ values. However, a detailed examination of the minerals has shown that definite ranges of composition are found and that the minerals of the family are properly divided into the generally accepted groups.

*The chlorite group:* $(Mg, Fe)_{6-p}Al_{2p}Si_{4-p}O_{10}(OH)_8$. Typical members of this group are as given in the following table.

TABLE 5. CHLORITES

| Orcel (1927) | | | | | | |
|---|---|---|---|---|---|---|
| page | no. | Name | $n$ | $p$ | $Mg/Fe''$ | $Al/Fe'''$ |
| 331 | 1 | Amesite | 6 | 1.6 | 2.25 | Al |
| 331 | 6 | Corundophilite | 6 | 1.6 | 6.5 | 12 |
| 192 | — | Sheridanite | 6 | 1.5 | 45 | Al |
| 346 | 35 | Colerainite | 6 | 1.4 | Mg | Al |
| 357 | 78 | Ripidolite | 6 | 1.45 | 1.9 | 7.5 |
| 247 | — | Bavalite | 6 | 1.46 | 0.09 | 52 |
| 221 | — | Grochauite | 6 | 1.35 | 10 | Al |
| 216 | — | Prochlorite | 6 | 1.37 | 5 | 67 |
| 228 | — | Ripidolite | 6 | 1.3 | 1.9 | 17 |
| 367 | 126 | Metachlorite | 6 | 1.3 | 0.2 | 4 |
| 347 | 38 | Rumpfite | 5.7 | 1.3 | 4.8 | 23 |
| 360 | 100 | Ripidolite | 6 | 1.4 | 0.51 | Al |
| 198 | — | Leuchtenbergite | 6 | 1.2 | Mg | Al |
| 201 | — | Prochlorite | 6 | 1.2 | 13 | 19 |
| 349 | 50 | Rumpfite | 6 | 1.18 | Mg | Al |
| 365 | 119 | Pycnochlorite | 6 | 1.15 | 1.1 | 13 |
| 365 | 120 | Delessite | 6 | 1.15 | 2.9 | 23 |
| 348 | 43 | Leuchtenbergite | 6 | 1.14 | Mg | 20 |
| 267 | — | Clinochlore | 6 | 1.08 | 12 | 15 |
| 382 | 185 | Brunsvigite | 6 | 1.05 | 0.47 | 14 |
| 269 | — | Crome clinochlore | 6 | 1.0 | 43 | 5.2* |
| 380 | 166 | Clinochlore | 6 | 1.0 | Mg | Al |
| 380 | 172 | Clinochlore | 6 | 1.0 | 6.9 | Al |
| 387 | 200 | Ripidolite | 6 | 0.83 | 11 | 25 |
| 387 | 202 | Pennine | 6 | 0.79 | 20 | 14 |
| 389 | 217 | Tabergite | 6 | 0.76 | Mg | Al Alkalies |
| 408 | 275 | Kotschubeite | 6 | 0.91 | Mg | 5* |
| 408 | 276 | Kammererite | 6 | 0.9 | Mg | 1* |
| 409 | 278 | Kammererite | 6 | 0.87 | Mg | 3.33* |
| 410 | 285 | Kammererite | 6 | 0.86 | 30 | 1.8* |

* Al/Cr.

The minerals listed above are representative, well analysed chlorites. The analyses examined are among more than two hundred collected by Orcel (1927). More than twice the number given above were examined, because of their apparent superiority among the many analyses found in Orcel's paper. All have not been included in this table because they do not properly fall here in the classification, since the value $n$ is less than 6. Tschermak (1890) recognized that chlorite-like minerals of a definitely different composition could not be grouped with the well-defined chlorites. These are here called Lepto-chlorites ($N<6$), as in Tschermak. Incidentally, the only important criticism of Orcel's work on the chlorites lies in his failure to recognize the significance of the variability of the divalent elements.

In order to define properly a member of the chlorite family it is necessary to give the values, $n$, $p$ and the ratios Mg/Fe″, Al/Fe‴. The relation of these quantities to Orcel's symbols are $s=(4-\mathrm{p})/\mathrm{p}$; $a=\mathrm{Fe}'''/\mathrm{Al}$; $f=\mathrm{Fe}''/\mathrm{Mg}$; where $s$, $a$, $f$, are symbols used by Orcel.

The relations to the Tschermak and Winchell symbols are:

$$50\ \mathrm{p}=\%\mathrm{At}=\mathrm{Amesite};\ 100-50\mathrm{p}=\%\mathrm{Ant}=\mathrm{Antigorite}.$$

It is to be noted that the terms used by the writer can be directly placed in the general formula for the group. Ths single term serves the purpose of the two end member terms of Tschermak, and bears a simpler relation to the composition than the term $s=\mathrm{SiO_2/R_2O_3}$ of Orcel. The term $p$, as the formula shows, is half the number of atoms of the (Al, Fe‴) kind in the composition. Since the (Al, Fe‴) content fixes both the Si and (Mg, Fe″) amounts, the single term is adequate.

In the above table a number of names usually associated with the chlorites, such as cronstedtite, thuringite, aphrosiderite, are missing. These are to be found on the following pages under the leptochlorites.

*The leptochlorite group:* $(\mathrm{Mg, Fe})_{n-p}(\mathrm{Al, Fe'''})_{2p}\mathrm{Si}_{4-p}\mathrm{O}_{10}(\mathrm{OH})_{2(n-2)}\cdot s\mathrm{H_2O}$. Table 6 lists the leptochlorites taken from Orcel's collected analyses. The group is divided into three sections in the classification, the divisions being made on the basis of significant $n$ differences. The first section is composed of chlorite-like minerals not very different from true chlorites. It may be that some of these minerals belong in the previous group and that the chemical analyses are somewhat defective. However, most of the minerals given are represented by recent analyses which are probably reliable. The second section shows a definite departure from the true chlorite composition not only in the $n$ value, but also in the fact that many of the minerals have a higher $p$ value than is found in the chlorites, and also much more Fe″ and Fe‴.

Cronstedtite, with the composition $\mathrm{Fe_3''Fe_4'''Si_2O_{10}(OH)_6}$ is totally unlike any mineral of the chlorite group in its composition. The thuringites are likewise definitely different chemically. It is worth noting here again that the species names, as given with the analyses, have not been changed, mainly because the writer is not inclined to enter here into a discussion of the suitability of certain names for specific portions of a series. In this paper the series is considered as the important unit, and the writer believes that the leptochlorites represent a more or less continuous series with the variations as indicated.

Whether there is a continuous series beteen the leptochlorites and the chlorite group cannot be shown by the chemical evidence. A serial relation seems, however, unlikely since the chlorites do have a definitely different composition and a constant *n* value. Further, optical properties of the leptochlorites do not fit well with the optics of normal chlorites. It is perhaps due to the failure to discriminate between the two groups that the optical properties of the chlorite group are so unsatisfactorily known.

A number of interesting possibilities for structural studies present themselves in the leptochlorites. It would be interesting to know whether the unit cell dimensions change in this group, as compared with the chlorites. Of greater interest is the mineral cronstedtite, $Fe_3''Fe_4'''Si_2O_{10}$-$(OH)_6$ or $(Fe_3''Fe_2''')(Fe_2'''Si_2O_{10})(OH)_6$, in which Fe''' is in the tetrahedral network and occupies half the positions, with Si in the other half. If true, this is the most important case of this sort in the silicates and there seems to be little doubt that this must be true, since no Al is available to enter into the network. It may be that this unusual condition in the tetrahedral network may account for the peculiar curved pyramid-shaped crystals of this mineral, for the network under these conditions would certainly be distorted.

TABLE 6. LEPTOCHLORITES

| Orcel (1927)<br>page | no. | Name | *n* | *p* | Mg/Fe'' | Al/Fe''' | *s* |
|---|---|---|---|---|---|---|---|
| 335 | 14 | Aphrosiderite | 5.5 | 1.55 | 2.34 | 3.75 | 0 |
| 236 | — | Ripidolite | 5.6 | 1.38 | 1.1 | 3.1 | 0 |
| 238 | — | Ripidolite | 5.6 | 1.38 | 1.3 | 8.0 | 0 |
| 358 | 88 | Ripidolite | 5.7 | 1.39 | 1.67 | Al | 0 |
| 367 | 125 | Chlorite | 5.3 | 1.52 | 0.4 | 8.3 | 1 |
| 368 | 132 | Daphnite | 5.3 | 1.43 | 0.05 | Al | 0 |
| 371 | 139 | Prochlorite | 5.5 | 1.34 | 0.7 | 4.75 | 0 |
| 375 | 155 | Cronstedtite | 5.7 | 1.35 | 0.2 | Fe''' | 0 |
| 367 | 129 | Chamosite | 5.5 | 1.2 | 0.09 | Al | 1 |
| 373 | 153 | Prochlorite | 5.7 | 1.1 | 1.0 | 3.8 | 0 |
| 382 | 180 | Delessite | 5.5 | 1.06 | 2.3 | 7.7 | 0 |
| 363 | 122 | Diabantite | 5.7 | 1.08 | 1.03 | 6.2 | 0 |
| 385 | 189 | Pseudophite | 5.5 | 0.9 | 50 | Al | 0 |
| 387 | 197 | Prochlorite | 5.6 | 0.86 | Mg | Al | 0 |

| Orcel (1927) | | | | | | | |
|---|---|---|---|---|---|---|---|
| page | no. | Name | $n$ | $p$ | Mg/Fe'' | Al/Fe''' | $s$ |
| 376 | 160 | Cronstedtite | 4.95 | 1.93 | Fe | Fe | 0 |
| 375 | 159 | Cronstedtite | 4.85 | 1.55 | low | Fe | 0 |
| 257 | — | Thuringite | 5 | 1.5 | 0.32 | 2.7 | 0 |
| 337 | 28 | Thuringite | 5 | 1.48 | 0.3 | 2.1 | 0 |
| 337 | 26 | Thuringite | 4.8 | 1.5 | 0.1 | 2.1 | 1 |
| 335 | 18 | Thuringite | 4.75 | 1.64 | 0.07 | 1.74 | 1 |
| 358 | 84 | Klementite | 5.2 | 1.5 | Mg | Al | 0 |
| 373 | 152 | Delessite | 5.2 | 1.15 | 1.6 | 5.5 | 1 |
| 385 | 188 | Pennine | 5 | 0.89 | Mg | 25 | 1 |
| 393 | 219 | Diabantite | 5 | 0.72 | 2.78 | 6.5 | 1 |
| 334 | 9 | Thuringite | 4.67 | 1.6 | 0.67 | 17 | 0 |
| 334 | 12 | Thuringite | 4.5 | 1.7 | 0.05 | 1.46 | $1\frac{1}{2}$ |
| 371 | 141 | Delessite | 4.6 | 1.28 | 1.8 | 3.5 | $1\frac{1}{2}$ |
| 264 | — | Thuringite | 4.4 | 1.77 | 3.2 | 2 | 0 |
| 336 | 22 | Thuringite | 4.37 | 1.58 | 0.17 | 1.85 | $2\frac{1}{2}$ |
| 368 | 136 | Prochlorite | 4.3 | 1.38 | 0.09 | Al | 2 |
| 395 | 234 | Epichlorite | 4.2 | 0.8 | 3.6 | 1.9 | 0 |
| 371 | 140 | Delessite | 4.1 | 1.34 | 8.4 | 1.4 | 1 |
| 382 | 184 | Aphrosiderite | 4 | 0.93 | 0.62 | 100 | 0 |

The vermiculites are, as stated before, chloritic minerals with a high water content, the latter probably accounting for the peculiar expansion properties. Saponite has not hitherto been placed with the vermiculites, but its chemical and physical properties indicate that it might well be considered a vermiculite-like mineral. Griffithite has been placed here for the same reason. The $n$ values indicate that the unit cell must have at least three times the number of atoms here given in the formula, since any unit cell should have an integral number of $n$ atoms. However, to show better the relations with other members of the family the fractional values of $n$ are retained.

*Brittle mica family:* The minerals here listed are much like those of the chlorite family in that the same general formula applies to them and the same elements enter into their composition, except that Ca is found in considerable amounts in some members. It is to be noted, however, that the $n$ values in these minerals are considerably lower than those found in the chlorite family, as is also the water content.

Physically these minerals differ from the chlorite family in being harder and, as the name of the family implies, more brittle. The cleavage is perhaps somewhat less perfect than in the chlorites. Optically some of these minerals differ from the other platy silicates in that the positive acute bisectrix emerges almost normal to the perfect cleavage (ottrelite, chloritoid, prehnite).

Chalcodite $(Mg, Fe)_{13}Al_4Si_{18}O_{50}(OH)_{10} \cdot 10H_2O$. The writer follows Hallimond (1924) in separating the two species, chalcodite and stilpnomelane. The chalcodites are definitely lower in $Al+Fe'''$ and higher in $Mg+Fe''$ (Analyses 7a and 7b in Hallimond's paper). There are at least five times as many atoms in the unit cell of chalcodite as we have given in the general family formula in the classification.

Epichlorite $(Mg, Fe)_{10}Al_6Si_{13}O_{40}(OH)_{10} \cdot 8H_2O$ yields the value $n$ and $p$ as given in the classification. The formula indicates that there are at least four of the general formulae in a unit cell (analysis number 233 in Orcel).

Stilpnomelane $(Mg, Fe)(Al, Fe''')_2Si_3O_{10} \cdot H_2O$. From a consideration of analyses in Hallimond's paper the simple formula is deduced for stilpnomelane. This mineral probably forms a series with certain of the ottrelites which differ only in having more $Fe''$ and some $Mn''$ in their composition (see classification).

Ekmannite is presumably similar in composition to members of this group. However, more chemical work is needed definitely to establish this species.

Ottrelite $(Fe'', Mn)(Al, Fe''')_2Si_3O_{10} \cdot H_2O$. The six analyses for this species listed in Dana (1892, p. 642) give the following values of $n$, $p$, and $s$ (as used in the general formula):

| Dana number | $n$ | $p$ | $s$ |
|---|---|---|---|
| 1 | $2\frac{1}{2}$ | 1 | 1 |
| 2 | 2 | $1\frac{1}{2}$ | 1 |
| 3 | $2\frac{1}{2}$ | $1\frac{1}{4}$ | 0 |
| 4 | $2\frac{1}{2}$ | $1\frac{1}{4}$ | 0 |
| 5 | $2\frac{1}{2}$ | $1\frac{1}{4}$ | 0 |
| 6 | 2 | 1 | 1 |

A new analysis of this mineral is needed to establish its composition since the analyses available are not in good agreement with each other. The writer believes that ottrelite is essentially similar to stilpnomelane.

Margarite $CaAl_4Si_2O_{10}(OH)_2$. This is a well-defined species of simple composition. The recently described ephesite is a supposed soda-margarite of composition $(Na, Li, Ca)_2Al_4Si_2O_{10}(O, OH, F)_2$, with Li and Ca subordinate. This mineral is probably isostructural with margarite. Although the latter contains some Na, the amount is small, and no evidence is found of a large $Ca\text{–}Na_2$ substitution.

Prehnite $Ca_2Al_2Si_3O_{10}(OH)_2$ is not usually associated with the platy silicates. However, it often has a distinctly platy habit, when in crystals; the basal cleavage is good, giving a pearly luster, and the acute bisectrix is normal to the plane of platy development. The platy cleavage is not inferior to that found in chloritoid or ottrelite, of this section. According to Pauling (1930 A) the Ca members of the platy silicates should be the ones showing the least perfect cleavage and the greatest hardness because the bivalent Ca bonds interfere with easy separation of the layers.

Chloritoid $(Fe, Mg)_2Al_4Si_2O_{10}(OH)_4$, is chemically a rather well-defined brittle mica, not far removed in its composition from some of the leptochlorites. As much as 8 per cent of Mn is present in salmite, a manganiferous chloritoid. Most chloritoids carry some Mg, but Fe is the predominant constituent.

Clintonite series $X_4Z_4O_{10}, (OH)_2$ with $X = Mg:Ca:Al = 3:2:1$; $Z = Al:Si = 2:1$. The formula expanded yields $Mg_6Ca_4Al_{10}Si_4O_{30}(OH)_6$. This is the composition of the supposedly different species seybertite, brandisite, and xanthophyllite. The analyses as given for these three minerals (Dana, 1892, p. 638) indicate that they differ only in the Mg:Ca ratio, if at all. However, the difference in this ratio is no greater between the species than it is between different analyses of the same species. Since the composition of the three minerals is established on old analyses (1847, 1853, 1887) on material not definitely shown to be pure, the writer is inclined to consider that the variation in the Mg:Ca ratio is not sufficient to retain three species names for this single series.

Kossmatite, a recently described mineral, has a composition $X_6Z_4O_{10}(OH, F)_9$, with $X = Ca:Mg:Al = 3:1:2$; $Z = Al:Si = 1:3$; giving $Ca_3MgAl_3Si_3O_{10}(OH, F)_9$.

*Mica group:* $W(X, Y)_{2-3}Z_4O_{10}(O, OH, F)_2$; W = K predominantly, Na, Ba, Ca subordinate to rare; X = Mg, Fe'', Mn'', Li; Y = Al, Fe''', Ti subordinate, Cr, Mn''', V rarely; Z = Si:Al from 5:3 to 7:1.

|  | *X* | *Y* | *Z*=16 Al:Si | OH:F | Formula |
|---|---|---|---|---|---|
| *Muscovite series:* |  |  |  |  |  |
| Muscovite |  | 8 | 2:6 | 8:0 | $K_4Al_{12}Si_{12}O_{40}(OH)_8$ |
| Phengite | 2 | 6 | 1:7 | 8:0 | $K_4Mg_2Al_8Si_{14}O_{40}(OH)_8$ |
| Alurgite | 3 | 5 | 1:7 | 9:0 | $K_4Mg_3Al_7Si_{14}O_{39}(OH)_9$ |
| Paragonite |  | 8 | 2:6 | 8:0 | $Na_4Al_{12}Si_{12}O_{40}(OH)_8$ |
| Roscoelite |  | 8 | 2:6 | 8:0 | $K_4V_8Al_4Si_{12}O_{40}(OH)_8$ |
| *Biotite series:* |  |  |  |  |  |
| Biotite | 12 |  | 2:6 | 8:0 | $K_4(Mg, Fe)_{12}Al_4Si_{12}O_{40}(OH)_8$ |
| Phlogopite | 12 |  | 2:6 | 8:0 | $K_4Mg_{12}Al_4Si_{12}O_{40}(OH)_8$ |
| Siderophyllite | 10 | 2 | 3:5 | 8:0 | $K_4Mg_{10}Al_8Si_{10}O_{40}(OH)_8$ |
| Biotite? | 8 | 4 | 2:6 | 4:0 | $K_4(Mg, Fe)_8Al_8Si_{12}O_{44}(OH)_4$ |
| Biotite? | 10 | 2 | 2:6 | 6:0 | $K_4(Mg, Fe)_{10}Al_6Si_{12}O_{42}(OH)_6$ |
| *Lithia Micas:* |  |  |  |  |  |
| Lepidolite | 8 | 4 | 2:6 | 4:4 | $K_4Mg_4Li_4Al_8Si_{12}O_{40}(OH)_4F_4$ |
| Lepidolite | 6 | 6 | 1:7 | 4:2 | $K_4Li_6Al_8Si_{14}O_{42}(OH)_4F_2$ |
| Lepidolite | 6 | 5 | 1:7 | 2:7 | $K_4Li_6Al_7Si_{14}O_{39}(OH)_2F_7$ |

| | | | | | |
|---|---|---|---|---|---|
| Zinnwaldite | 8 | 4 | 2:6 | 4:4 | $K_4Fe_4''Li_4Al_8Si_{12}O_{40}(OH)_4F_4$ |
| Polylithionite | 8 | 4 | 0:8 | 0:8 | $K_4Li_8Al_4Si_{16}O_{40}F_8$ |
| Cyrophyllite | 8 | 4 | 1:7 | 2:6 | $K_4Fe_2''Li_6Al_6Si_{14}O_{40}(OH, F)_8$ |

The muscovite series consists of members which are predominantly Al and Si compounds, with little Mg and Fe″, and rarely any F. Ba and Na replace some of the K, but rarely in notable amounts (except in paragonite). Special members of this group are fuchsite with small amounts of Cr replacing Al, and roscoelite with most of the Al replaced by V. Phengite and alurgite are members in this series having a larger than usual amount of Si.

The biotite series comprises those members wherein considerable amounts of Mg and Fe″, sometimes Mn″ in manganophyllite, are present, and part of the Al is replaced by Fe‴ and Mn‴ and minor amounts of Ti.

The lithia micas are those which have much Li and considerable F in place of OH.

The chief members of these mica series are arranged to show their variation, according to the formula. It must be noted in this connection that the X and Y portions of the formula are especially variable and consequently give rise to many compositions intermediate between those given here. Although there are probably hundreds of mica analyses, complete agreement as to the composition of some of them, especially in the Lithia mica groups, has not yet been reached. The formulae presented above are in good agreement with the analyses as well as with the structural relations established for the micas. These are, with some exceptions, in essential agreement with Winchell's latest conclusions, as expressed in his book (1933), but not with the conclusions of his earlier papers on the micas. Hallimond's views on the micas (1925) are not accepted.

The many recent analyses by Kunitz (1924) and Jakob (1925) have been utilized in this study. Early analyses of the micas were especially likely to be faulty since fluorine was often missed.

The structure of muscovite (Jackson and West 1930) has been fully determined. The lithia micas are most in need of structural investigation because the muscovite structure certainly needs some modification in order to meet the compositional differences of the lithia members of the group.

Since most of the examined analyses of the micas fall into some intermediate position in one or the other of the series given above, more details are not given here. The members of the series as given are to be considered as expressing the principal variations found. The species names are those originally used with the particular analysis from which the formula was derived.

*Miscellaneous disilicates:* Glauconite $W_2(X, Y)_8(Z_4O_{10})_3(OH)_{12}$; $W=K$, Na subordinate; $X=Mg$, $Fe''$; $Y=Al$, $Fe'''$; $Z=Si$. More specifically the composition is $K_2Mg_2Al_6(Si_4O_{10})_3(OH)_{12}$. The composition of this mineral has been recently studied (Schneider 1927; Ross 1926; Hallimond 1922) and Gruner (1935 B) has proposed a structural arrangement similar to that of the micas.

Pholidolite is a mica-like mineral having a deficiency of K and an excess of water; it is probably an alteration product of a mica. Its formula is $KMg_6AlSi_7O_{20}(OH)_4 \cdot 3H_2O$; or $WX_6(Z_4O_{10})_2(OH)_4 \cdot 3H_2O$. This general formula, it will be seen by comparison, is not far from the mica formula.

Cookeite is a micaceous silicate having the composition: $LiAl_3Si_2O_9+3H_2O$. Expressed as a platy silicate it gives the formula: $(XY)_4(Z_4O_{10})(OH)_4 \cdot 2H_2O$; with $X:Y=Li:Al=1:2$; and $Z=Al:Si=1:2$.

Manandonite is presumably closely related to cookeite but has some oron in the composition.

Bityite $W_4(X, Y)_{12}(Z_4O_{10})_3(OH)_{20}$; $W=Ca$; $Z=Al:Si=1:2$ $(X, Y)=Li:Be:Al=2:1:6$; or $Ca_4(Li, Be)_4Al_8[(Al, Si)_4O_{10}]_3(OH)_{20}$.

Ganophyllite. An analysis of the light brown ganophyllite from Franklin (private contribution, L. H. Bauer 1936) yields the composition: $NaMn_6Al_2(Si_4O_{10})_2(OH)_{11}$. A recent description (Foshag 1936) of a somewhat different ganophyllite gave the composition $(Na, K, Ca)_2Mn_6Al_3Si_{10}O_{32} \cdot 8H_2O$. These two compositions do not, in the writer's opinion, represent the same mineral. The mineral described by Foshag is perhaps more appropriately placed in the brittle micas, or the related leptochlorites. A further study of the two occurrences at Franklin should be made in order to reach some conclusion concerning the true constitution of ganophyllite.

## Metasilicate Type

The metasilicates are those silicates which have a ratio of $Z:O=1:3$, where Z is in most instances Si alone, and sometimes Si+Al with Si greatly predominating; O represents not only oxygen but OH, and F in small amounts. These silicates are divided into two principal subtypes, (A) the chain structure subtype, and (B) the ring structure subtype. The minerals with chain structures have Mg, $Fe''$, Ca, Mn, Al and $Fe'''$ as the important elements of the composition. Those with the ring structures have the relation $Z:O=n:3n$, with $n=3$ or 6, and are, in general, more unusual in their chemical composition. The members with chain structures are all characterized by a distinct prismatic habit which often takes the accentuated fibrous form. This development is a consequence of the internal structure, which is the linking of tetrahedra to form continuous chains throughout the crystal. Presumably the chief differences in the various members of this type are due to the way the chains are tied together. Warren and Biscoe (1931) have demonstrated the relations between the pyroxenes and amphiboles in this respect. The full structural details of other chain structures are not yet known.

The ring structures are formed by $SiO_4$ tetrahedra joined in groups of three, as in benitoite (Zachariasen 1930 B), or in groups of six as in beryl (Bragg and West 1926). Some of the minerals grouped here are as yet not determined structurally. All the minerals placed in the ring structure type have trigonal or hexagonal symmetry, which is consistent with the structure of this type.

*Amphibole group:* There are, as shown in the classification, four distinct series in the amphiboles. Within each series there is isomorphism to the extent indicated in the formulae, but between these series little overlapping is found. Since Berman and Larsen (1931) have already discussed the composition of this group in some detail, the main points only need be cited here.

Anthophyllite and cummingtonite differ not only in crystal symmetry but also in that the orthorhombic members are high in Mg, and the monoclinic cummingtonite relatively high in $Fe''$.

The tremolite-actinolite series is perhaps the best known in the amphiboles. It was in this series that the importance of water in the amphibole composition was first recognized (Schaller 1916). Most of the members of this series are relatively high in Mg. Few reliable high $Fe''$ actinolites have been reported.

The hornblende series is perhaps the most complex series in the silicates. It varies more or less continuously with respect to the ratios $Ca/Na$, $Mg/Fe''$, $Al/Fe'''$, $Al/Si$ and $OH/F$. Most of the variations mentioned have been actually found in the amphiboles, of which there are hundreds of analyses. In view of this remarkable isomorphism, it is no wonder that so many species names have been proposed for members of the hornblende series. Unfortunately, some of the names in the literature are based on habit, or optical properties. For our purpose these names are of no value, since our classification is chemical and structural, and any other basis of classification cannot consistently be superimposed on it.

The species listed are fairly representative of the range in the series, but it must again be pointed out that this is not a list of so-called end members. It is a list of the most commonly found compositions in the series.

Narsarsukite $Na_8FeTi_3Si_{16}O_{43}F$, or $W_2X\ Si_4(O, F)_{11}$ has been shown by Warren and Amberg (1934) to be of this composition, and is presumably of a structural type closely related to the amphiboles.

Chrysotile $X_6Si_4O_{11}(OH)_6 \cdot H_2O$; $X=Mg$ predominantly; Fe″minor amounts; Ni, Mn subordinate; Al small amounts. The species name chrysotile is here applied only to the fibrous mineral of this composition; another name which might equally well be used is serpentine. Serpentine has been shown to have the chain structure (Warren and Bragg 1930). The so-called antigorite (see previous structure type) is platy and presumably of the same composition as serpentine. These two substances are apparently dimorphous.

*Pyroxene group:* The pyroxenes are, in general, a well-understood group of minerals, mainly because of their relatively simple chemical composition. The similarity of composition and physical properties of the pyroxenes and amphiboles have been stressed in the textbooks. Actually, the compositions of the two groups are as widely different as almost any two groups in a particular silicate type. Warren and Biscoe (1931) have shown that the two structures are related in a rather simple way.

The orthorhombic enstatite-hypersthene series ranges from the pure Mg member to iron-rich hypersthenes with $Fe:Mg<1$. The Fe end component is not known in nature. Small amounts of Al and Ca, and less often Ti, are present in some hypersthenes.

The pigeonite series ranges between clinoenstatite, an artificial monoclinic mineral of the composition of enstatite, and a somewhat calcic member called pigeonite. No evidence of a natural series extending from clinoenstatite to diopside has as yet been presented. Few good analyses of pigeonite are available.

The diopside-hedenbergite series is well established throughout the range Mg–Fe″. Rarer members of the series contain Mn, Zn, Cr, in addition to the usual Mg, Fe″. The so-called Tschermak molecule is an expression of the amount of Al present in this series. Because the oxygen is constant in the unit cell of the pyroxenes (as it is in most silicates) an introduction of Al into a diopside means that this Al must be shared equally by the Mg-like atoms and by the Si; otherwise the valence demands would not be satisfied. The member of the series having an Al substitution of this sort is called augite.

The Tschermak molecule was written as $CaAl_2SiO_6$, or $CaAl(AlSiO_6)$. This sort of "molecule" implies that half the Si could be replced by Al in the chain network. No actual pyroxene approaching this composition has been found in nature. This "end member" has therefore not been accepted.

The acmite-jadeite series is probably continuous through the Al–Fe‴ range and shows a relationship to the diopside series, with intermediate members such as aegirite.

Spodumene is a monoclinic pyroxene from all the available evidence. However,it forms no ismorphous series with other members of the pyroxene group, and Li is rarely reported in a pyroxene analysis. While we have placed spodumene in the pyroxene group, we must recognize that the other members are more closely related to each other structurally than is spodumene to any of them.

The so-called "triclinic pyroxenes" are not included here in the pyroxenes because the writer believes they are more properly considered as a separate group, with no isomorphous relations to any of the pyroxene minerals, and with physical and chemical properties clearly differing from those of the pyroxenes. To these pyroxene-like minerals we here give the name pyroxenoids.

*The pyroxenoid family:* The comparatively simple metasilicate composition, together with the fibrous or prismatic development of the pyroxenoid minerals, suggest strongly that a chain structure is the most likely internal arrangement. Chemical and physical analogies with the pyroxenes further suggest that the structure of these minerals should be somewhat similar to that of the pyroxenes. Because of the low symmetry no complete structural solution of any of the pyroxenoids has as yet been presented.

As shown in the table, there are two well-defined groups in the pyroxenoids, and a miscellaneous group of minerals, more or less related. The rhodonites are sufficiently close in their relations to be considered a series. The wollastonite group shows little variation in the composition of its individual members and is therefore not a series.

The rhodonite series has the simple metasilicate composition given in the classification. Rhodonite is the most important member of the series, the others are probably isomorphously related with part of the Mn replaced by a small amount of Ca, some Zn in fowlerite, Fe″ in iron rhodonite and Mg, Fe″ in sobralite. Sundius (1931) has shown the close optical and chemical relations between these minerals. Ca is not present in considerable amounts in this series, but in the wollastonite group Ca is essential.

The wollastonite group is much more complex chemically than is the preceding series. In order to show better the variations in the composition of the members of the group the full cell contents (as determined by Warren and Biscoe 1931 for wollastonite) are used in the formulae. The wollastonite group of minerals does not form an isomorphous series, but most of the members are constant in composition. Although wollastonite and pectolite are probably isostructural, no intermediate compounds are known. Margarosanite is chemically intermediate between wollastonite and alamosite, but its crytal form is like neither of them and it cannot be considered as an isomorphous mixed-crystal of a series.

The mineral bustamite $CaMnSi_2O_6$ has been assumed to be an end component of a rhodonite-bustamite series. However, it is not so placed here because, (1) *x*-ray powder patterns indicate that bustamite is more closely related structurally to wollastonite than to rhodonite (Bowen, Schairer and Posnjak 1933); (2) no continuous variation in the physical properties has been shown to exist in a presumed bustamite-rhodonite series; (3) Sundius has pointed out optical similarities between bustamite and wollastonite. A more detailed *x*-ray study of bustamite by the writer using cleavage prisms of the mineral has shown that the lattice constants of bustamite are close to those of wollastonite (paper read before the Mineralogical Society, 1936).

The compositions of wollastonite and pectolite present a problem in structural analysis. The two are related as follows:

| | |
|---|---|
| Wollastonite | $Ca_6\ Si_6\ O_{18}$ |
| Pectolite | $Ca_4Na_2\ Si_6\ O_{16}(OH)_2$ |

In pectolite the ratio $Si:O=3:8$, in wollastonite it is $3:9$. If the two are isostructural, the chain must have either an $Si_3O_8$ or an $Si_3O_9$ composition for both minerals. In the former case, the most likely, the oxygen atoms of wollastonite are of two kinds; 16 are in the tetrahedral network and 2 are not. In the other alternative, $Si:O=3:9$ (or $6:18$), the (OH) of pectolite would necessarily be in the tetrahedral network. This is unusual for silicates, although it has previously been reported (Zachariasen 1931). In a recent paper on the structure of wollastonite Barnick found that none of his chain arrangements would satisfy the *x*-ray data.

Alamosite is monoclinic (Palache and Merwin 1909) and shows only a partial relation to the triclinic wollastonite group. An intermediate mineral, margarosanite, is not similar crystallographically or in habit to either of the above mentioned minerals, and it cannot be placed in a series with them.

Under miscellaneous pyroxenoids are listed several minerals which have some relation, either in crystallography or in composition, or both, to the first two pyroxenoid groups.

Babingtonite is a mineral of definite composition and crystallographic properties close to those of rhodonite (Gossner and Brückl 1928). The composition would not lead one to expect a close structural relation between the two; yet Richmond (1937) shows that the two species have closely similar triclinic lattices, and are probably isostructural. The extent of the similarity of composition can be shown by comparing the cell formulas:

Rhodonite: $Mn_{10}Si_{10}O_{30}$
Babingtonite: $Ca_4Fe_2''Fe_2'''Si_{10}O_{28}(OH)_2$

If these two species are isostructural, two positions in the cell of babingtonite are vacant where two manganese atoms would be found in the rhodonite cell.

Taramellite is a rare silicate, essentially a Ba babingtonite in composition. It is said to be orthorhombic in symmetry, and to have no $H_2O$ in its composition so that it is probably not isostructural with babingtonite.

Hyalotekite is one of the rare Långban minerals, with a metasilicate composition and cleavages indicating a relationship to some of the minerals of this section.

Neptunite is a simple metasilicate of a composition and form not unlike the pyroxenoids or the pyroxenes. The Ti is not grouped here with the Si because the usual co-ordination number of Ti is not the same as that of Si in the silicates. In the formula for neptunite given in the classification $Fe''+Mn''$:Ti is 1:1.

The calcium metasilicates are of fibrous habit, rarely forming crystals suitable for measurement; data for these minerals are consequently scarce. Of those listed xonotlite has been studied by the writer crystallographically and by use of *x*-rays, and analysed recently by Bauer (in Palache 1935). Xonotlite is monoclinic and shows a relation to wollastonite in its unit cell dimensions. With two units of the formula $Ca_3Si_3O_8(OH)_2$ in the cell, the $b_0$ and $c_0$ values of wollastonite and xonotlite are almost identical. The $a_0$ value of xonotlite is somewhat greater than is the $a_0$ of wollastonite, as shown below:

| | | | | |
|---|---|---|---|---|
| Wollastonite | (Warren) | $a_0=7.88$Å; | $b_0=7.27$Å; | $c_0=7.03$Å |
| Xonotlite | (Berman) | $a_0=8.55$Å; | $b_0=7.34$Å; | $c_0=7.03$Å |

Wollastonite is triclinic and xonotlite is definitely monoclinic despite the fact that $\beta$ is 90°. Both minerals are elongated in the *b*-axis. There is little doubt that these minerals are structurally related, and perhaps both are made up of $Si_3O_8$ chains, for the xonotlite formula clearly suggests this type of chain. One might hazard the guess that the extra (OH) of the xonotlite lies along the *a*-axis, since that is the direction in which the cell is slightly increased in size over that of wollastonite.

Inesite is, as the formula indicates, closely related to xonotlite chemically. However, it is triclinic and differs optically from xonotlite.

The mineral foshagite has been shown to be identical with hillebrandite. This has been checked independently by the writer.

Jurupaite is presumably an equivalent of riversideite with the Ca:Mg ratio of 7:1. These are finely fibrous minerals and exact data for them is lacking.

*Copper metasilicates:* The copper metasilicates are all finely fibrous to cryptocrystalline. Chrysocolla is often amorphous and rather variable in composition. The other minerals of this family seem to have distinct optical properties and are therefore valid species.

*Miscellaneous metasilicates.* The chief reason for placing this list of miscellaneous minerals here is that they are fibrous or prismatic and their compositions can be expressed as metasilicates. They vary widely in their physical properties and have little in common. A division is made between those having the composition $(SiO_3)_n$ and the five minerals at the end of the list with a composition $(Si_3O_8)$ (see pectolite and xonotlite). These latter minerals probably belong most properly in the metasilicate chain division of the classification, although their composition suggests a more complex chain arrangement than that of the other metasilicates. Some evidence of a complex chain has been presented for eudidymite and epididymite; the others have not been studied structurally.

*Ring structures of the metasilicate type*

| | |
|---|---|
| Benitoite | $WYZ_3O_9$ |
| Catapleiite series | $WYZ_3O.2H_2O$ |
| Eudialyte series | $W_2(X, Y)Z_3O_8(OH, Cl)$ |
| Steenstrupine | $W_4XY_6(Z_3O_9)_3(OH)_7 \cdot 3H_2O$ |
| Tourmaline | $WX_3Y_6(Z_3O_9)_3(O, OH, F)_4$ |
| Beryl | $X_3Y_2Z_6O_{18}$ |

The minerals of this sub-type have as their principal structural feature the closed metasilicate ring (Fig. 4, c, e). Benitoite and beryl have been studied and their structures show the two kinds of rings found, one of three tetrahedra to form a trigonal pattern, and the other of six to form the hexagonal pattern of beryl. From the structure data one would expect other members of this type to be either hexagonal or trigonal (or nearly so, in the case of pseudosymmetry). The members here listed are for the most part trigonal and thus far they fit the requirements. For those which have not been studied structurally the writer can only say that heretofore no simpler formulae have been proposed, and no adequate place in any classification has been found for these complex silicates.

Benitoite $BaTiSi_3O_9$. Zachariasen (1930B) has established the ring structure for this mineral.

Catapleiite series $(Na_2, Ca)ZrSi_3O_9 \cdot 2H_2O$. Catapleiite is pseudohexagonal at room temperature and hexagonal at 140°C. The formula is derived from the analyses in Dana (1892, p. 413). Natron-catapleiite gives the composition: $Na_2ZrSi_3O_9 \cdot 2H_2O$, which is much like that of eudialyte. Apparently in the ordinary catapleiite Ca substitutes for $Na_2$, a rather unusual substitution in the silicates where atom-for-atom replacement is the rule.

Eudialyte (eucolite) series $(Ca, Na)_2(Zr, Ce, Fe'', Mn'')Si_3O_8(OH, Cl)$. The composition of the series is much like that of catapleiite. The chief difference is the partial replacement of the Zr of catapleiite by Ce, Fe, Mn in eudialyte. In addition some Cl is found in eudialyte.

Steenstrupine $CaNa_3Mn(Ce, La, Al, Fe''')_6(Si, Ti)_9O_{27}(OH)_7 \cdot 3H_2O$. This complex mineral is not closely related chemically to the minerals just described. However, its composition can be expressed in the above formula. The Ti in small amount probably here enters into the tetrahedral network, as it probably also does in some garnets.

*Tourmaline series:* Tourmaline is the most complex of the minerals placed in this type. The composition of tourmaline has been thoroughly investigated over a long period. However, no generally accepted expression of the composition has as yet appeared. A ring structure in which the principal elements of the composition are arranged to give the trigonal symmetry is, in the writer's opinion, the most logical initial assumption to be made. The formula above offers strong confirmation of this assumption since the principal groups of atoms are actually grouped in sets of 3. It is to be noted also that the important variations in the composition of the tourmalines are all contained in the single term X of the formula, i.e., one can define a tourmaline simply by giving the Ca/Na ratio and the elements present in the X part of the formula. This interpretation of the tourmalines follows that of Larsen and Berman (1934, p. 247) and differs in detail from that of Kunitz (1929).

Beryl $Al_2Be_3Si_6O_{18}$ usually has this simple composition; some beryls, however, carry alkalies and water. One such analysis with considerable alkalies gave $(Li, Na, Cs)Be_{2\frac{1}{3}}\,Al_2Si_6O_{18} \cdot \frac{1}{2}H_2O$. Unfortunately few such complete analyses are available so that the role of the alkalies in beryl is not clear. Bragg and West (1926) concluded from a structural study that the alkalies and water were placed somewhere within the channels parallel to the *c*-axis and lying within the hexagonal ring of tetrahedra.

## PYROSILICATE TYPE

The pyrosilicates are those which have the $Si_2O_7$ composition, resulting from two tetrahedra sharing an oxygen atom. Chemically the minerals of this type are characterized by a lack of Al, so that Al tetrahedra are not found in the structure, except in gehlenite, a member of the melilite series. Furthermore, the atoms, other than Si and O, the W atoms of our classification, are generally large in radius. Such elements as Y, Sc, Ce, Ca, Ba, Pb are common in this type; Na and K are notably lacking; Be is sometimes present.

No specific physical characteristics distinguish the type. There is a tendency for the crystals of these minerals to be tabular, as in melilite, barysilite, hemimorphite and molybdophyllite. They are usually of high refractive index and high density as compared with silicates of the first three types, although this is not so much due to the structure as it is to the presence of such elements as Pb, Ba and some of the rare earths.

*Thalenite group:* Of the minerals in this group thortvietite is best known since Zachariasen (1930A) has worked out its structure. The others are related both chemically and physically.

*Melilite group:* The writer (1929) has discussed the chemical composition of the melilite group elsewhere. A complete series between åkermanite and gehlenite is known in nature, and has been produced in the laboratory (Buddington 1922). Na enters into the composition to a rather limited extent with the composition $CaNaAlSi_2O_7$ as the probable limit of the Ca-Na series.

Hardystonite has been shown (Warren and Trautz 1930) to be isostructural with melilite, and Zachariasen (1931) has pointed out the similarity of the cell dimensions of leucophanite with that of melilite. The minerals of this group are all tetragonal with the exception of leucophanite which is pseudo-tetragonal. The composition of leucophanite illustrates the possibility of F entering into the silicon-oxygen tetrahedron in place of one of the oxygens (Zachariasen).

*Barysilite group:* The three minerals of this group are closely related; barysilite is rhombohedral, the other two are hexagonal. The compositional relationship can best be shown by writing the formula for ganomalite as $[(Ca, Pb)_3Si_2O_7]_3 \cdot Pb(OH)_2$. There is no evidence, however, that the Pb has more than one structural position, and the writer prefers the formula as given in the classification.

*Hemimorphite family:* Hemimorphite has been shown to belong to this structural type (Ito and West 1932A). Bertrandite, a related mineral both crystallographically and chemically, has also been studied structurally but without much success (Ito and West 1932B; Wyckoff 1935, p. 117). Clinohedrite has undoubted chemical relations to these two minerals and is for that reason placed here. Cuspidine and its hydroxyl equivalent custerite, $Ca_4Si_2O_7(OH, F)_2$, are clearly of this chemical type. Complete crystallographic data are lacking for these minerals. Murmanite and molybdophyllite are rather platy in habit, like barysilite, but they cannot possibly be placed in the disilicate type. Since many of the minerals in this type are tabular to platy, it is believed that these two are undoubtedly pyrosilicates, with a composition analogous to the members of the hemimorphite family. The minerals put together here as a family are so grouped mainly because they show chemical similarities. No close crystallographic relations have as yet been found.

*Miscellaneous pyrosilicates.* Barylite has a comparatively simple composition. Harstigite is a rare silicate of rather complex composition placed here with some uncertainty.

Lawsonite is of some special interest since its composition is similar to anorthite plus water: $CaAl_2Si_2O_8 \cdot 2H_2O$. If this mineral were of the silica type, as it well might be considering its composition, it would certainly have a low specific gravity and low refractive index as all of that type do. On the contrary it actually is an especially hard mineral with a specific gravity of 3.09 and mean refractive index of 1.67. These properties immediately rule it out of the silica type. The writer and Professor Warren of the Massachusetts Institute of Technology attempted to derive a structure of this mineral beginning with the assumption that it was an $SiO_4$ type, i.e., independent tetrahedra as the fundamental framework. This study failed to establish the structure, and the writer's opinion is that lawsonite probably has an $Si_2O_7$ structure, for this seems to be the only remaining possibility. A dehydration curve to determine the role of water is essential to reach some satisfactory solution of the structure.

Danburite, with the composition of an orthosilicate $CaB_2Si_2O_8$ has presumably a pyrosilicate structure (Dunbar and Machatschki 1930) so that its formula may be written $CaB_2(Si_2O_7)O$. No other example of this sort has, as yet, been found among the silicates.

Astrophyllite has the somewhat complex formula given, for the originally analysed material and also for the more recently described occurrences of the Kola region. The ratio $Fe'' : Al : Ti = 11 : 1 : 3$ to $8 : 3 : 4$.

Aenigmatite. The formula of aenigmatite has recently (Fleischer 1936) been given in the pyrosilicate form, as $W(X, Y)_{13}(Si_2O_7)_6$ or more specifically $(Na, Ca)_4(Fe'', Ti, Fe''', Mg, Al)_{13}(Si_2O_7)_6$. Since the physical properties are not too well established and the chemical variation is considerable, there may still be some question as to the adequacy of the formula of aenigmatite. Rhönite is said to be a calcium-aluminum rich aenigmatite but the best formula from the analyses bears no very close relation to the latter.

## ORTHOSILICATE TYPE

The orthosilicates are those in which independent $SiO_4$ tetrahedra are the characteristic feature of the fine structure. No tetrahedron shares oxygen atoms with any other silicon-oxygen tetrahedron and the resulting ratio is Si:O=1:4. When the ratio is less than 1:4 it means that some of the oxygens of the structure are not in the tetrahedra. This last type therefore merges into non-silicate structures wherein the tetrahedra no longer play a dominant role, or even an important one, and the minerals can no longer be said to be silicates. The transition silicates are here called subsilicates. At the end of the classification it becomes difficult to draw the line. The mineral sapphirine, where less than a third of the oxygens are in the tetrahedra, should not perhaps have been included in a silicate classification.

The orthosilicates are chemically diverse and no particular tendency for certain elements to be absent is known. Na and K are notably scarce and the rare earth and other rare elements are notably present. Al is found in most of the members but not in tetrahedral co-ordination so that Al and Si do not substitute for each other in any minerals of the type.

The physical characteristics of the type are sufficiently definite to be of some diagnostic value in the classification. Most of the minerals placed here have no pronounced tendency to form fibrous or platy crystals; they generally form equidimensional crystals. This is in keeping with the structural features of the type which does not have extended units of structure. The members of the type are generally hard and of comparatively high specific gravity, since the chief elements in the composition are the denser atoms and the packing is close. The refractive indices of most of the members are also comparatively high, for the same reasons.

*Chrysolite group:* The olivine series has within it eight well-defined species corresponding to the principal variations within the series. In addition, three other species, listed in the classification, are recognized. All of the elements, excepting Ca and Pb, form continuous series with each other. The limit of miscibility of Ca in the olivines is as shown in such minerals as glaucochroite, $CaMgSiO_4$. A Ca end component, larnite, is apparently not a member of the olivine series (Tilley 1929). Larsenite, $PbZnSiO_4$, is an unusual member, with Pb replacing the Ca part of the regular formula. A pure Zn member of this series is unlikely since the pure Zn orthosilicate formed in nature is the rhombohedral mineral willemite. The olivine structure (Bragg and Brown 1926) shows the structural non-equivalence of the two types of Mg atoms, one of which may be replaced by Ca without unduly distorting the lattice. This explains the limited miscibility of Ca in the series.

The two species larnite and merwinite are not closely related to the olivine series crystallographically, but they have the same type of composition. Larnite, $Ca_2SiO_4$ is, as expected from the structural evidence previously stated, not an olivine. The other mineral is equally rare and little is known of its properties.

*Phenakite group:* Phenakite and willemite are definitely related in both crystallographic and chemical properties. Dioptase, while it is close to the other two crystallographically, is less definitely related in its composition. No adequate structural work has as yet been done on dioptase. It would be particularly interesting to know the role of water in this mineral. The three minerals are in no sense a series since no mixed-crystals are known. Willemite does have some Mn in varying amounts in its composition, but some analyses are misleading because of the probable admixture of tephroite or some other Mn mineral. Trimerite (Mn, Ca)$BeSiO_4$ is pseudohexagonal and probably related in structure to the members of the phenakite group.

*Humite group:* To show the inter-relations of these minerals, their formulae may be written together with the forsterite formula, in a manner somewhat different from that given in the classification.

| | |
|---|---|
| Forsterite | $Mg_2SiO_4$ |
| Norbergite | $Mg_2SiO_4 \cdot Mg(OH, F)_2$ |
| Chondrodite | $2Mg_2SiO_4 \cdot Mg(OH, F)_2$ |
| Humite | $3Mg_2SiO_4 \cdot Mg(OH, F)_2$ |
| Clinohumite | $4Mg_2SiO_4 \cdot Mg(OH, F)_2$ |

It has been found by *x*-ray studies that this remarkable group is structurally composed of segments similar to the olivine structure with interleaved segments of brucite layers $Mg(OH)_2$. Since these are packed in the direction of the *c*-axis, the length of that axis changes from one species to the other in a regular way, but the other two axes are essentially constant in absolute length. A detailed account of the structure may be found in Taylor and West (1928) and Taylor (1929).

Dana (1892, p. 534) shows that these species have essentially the same *a*- and *b*-axes and that the *c*-axes are proportional to the number of Mg atoms in the formula, as 5:7:9 for chondrodite, humite and clinohumite respectively. The early crystallographic work thus anticipated in a measure the structural features found later.

*Hodgkinsonite group:* This group, in which no series are formed, is chemically similar to the preceding humite group, with Mn playing the role of Mg. The crystallographic and structural features of the group have not as yet been investigated from this point of view. Gageite is less certainly related to the group but it has no closer affinities and is therefore placed here.

*Garnet group:* The garnets have been studied from all points of view, and it is well recognized (Ford 1915) that there are two important series, as indicated above. For convenience in designating the series the most prominent members of each are here chosen (Winchell 1933, uses Pyralspite and Ugrandite). There is a small amount of miscibility between the two series, while the members of each series show a more or less complete range of miscibility. However, in the almandite series Mg and Fe show mixed crystals in all proportions, Fe'' and Mn through a wide range, but Mg and Mn do not form mixed crystals throughout the range. In the andradite series Al and Fe''' are completely miscible, whereas Cr is only present in small amounts in mixed crystals. Rarer constituents such as Mn''' and Ti enter into some of the garnets in small amount. Ford (1915) has discussed the miscibility ranges in the garnets at some length.

Titanium garnets, the so-called schorlomites, are comparatively rare and very few modern analyses are available for study. There seems to be little doubt, however, that Ti substitutes in part for Si in the composition. This may be explained perhaps by assuming that the larger Ti atom may fit into the tetrahedral framework at the high temperature of formation of these garnets. The formula derived from the most recent analysis (Hoffman 1901) is as given in the table above. Here $Si:Ti=2:1$, with Fe''' high as in most Ti garnets.

Sarcolite has a composition almost identical with that of grossularite. It is, however, tetragonal and has a very much lower refractive index and specific gravity. Little Na enters into the composition so that this slight variation cannot explain the physical differences. As a consequence of its comparatively low refractive index (1.61) and low specific gravity (2.9) the writer is not inclined to consider this mineral as a true orthosilicate. However, no better place in the classification is apparent. Certainly sarcolite has little in common with the scapolites with which it has been grouped (Gossner and Mussgnug 1928). The proper placing of this mineral must await an *x*-ray study.

Vesuvianite is variable in composition and a complete solution of its constitution is not yet available. Warren and Modell (1931) have investigated the complex structure and concluded that this mineral is related structurally to the garnets. Their study indicates that both $Si_2O_7$ and $SiO_4$ types of silicate structure are in the vesuvianite network. This is one of the few known structures where two types are found. An examination of the vesuvianite analyses shows that the formula given by Warren is not completely satisfactory. However, no better has been derived as yet, and Warren's formula is used here. The peculiar beryllium bearing vesuvianite recently described from Franklin, N. J. does not fit in any sense into the Warren formula, or any other which has ever been proposed for vesuvianite.

*Epidote group:* This group consists of an orthorhombic member, zoisite, which varies little from the composition given, and the more important monoclinic members which show considerable variation in composition. The group is divided into three series between which there is apparently no miscibility.

The epidote series has a little Mn″ in its composition (manganepidote); otherwise W is always Ca. Y is predominantly Al with a maximum of 40 atomic per cent of Fe‴; thus $Al:Fe''' \geqq 3:2$. In piedmontite Mn‴ represents as much as one-half the Y component.

In the allanites, rare earth elements as well as Mg, Be, and Na enter into the composition. An allanite having considerable Mg (magnesium orthite) has been described (Geijer, 1926). Another allanite of unusual composition is nagatelite (Iimori, 1931), in which part of the Si is replaced by P in the ratio $Si:P=5:1$. The possibility of this kind of replacement in the silicates has been discussed by Machatschki (1931).

Hancockite is a rare member of the epidote group with Sr and Pb in its composition.

Pumpellyite, a recently described mineral (Palache and Vassar 1925) differs from epidote chemically in having an extra molecule of $H_2O$. In some of its physical properties it resembles the epidotes, but crystals are not available for study. An *x*-ray investigation of the fibers would probably yield data adequate for comparison with epidote.

Sursassite $Mn_5Al_4Si_5O_{21} \cdot 3H_2O$ (Jakob 1926) has optical properties near those of a manganese epidote (Barth and Berman 1930). In view of the complexity of the given composition and its total dissimilarity from that of epidote, it would seem desirable to reinvestigate this mineral.

| *Zircon group* | $XSiO_4$ |
|---|---|
| Zircon | $ZrSiO_4$ |
| Thorite | $ThSiO_4$ |

The two minerals of this group are closely related in form, but no intermediate members are known. Zircon is essentially pure $ZrSiO_4$ with spectroscopic traces of many rare elements including Hf; Fe‴ is often reported in small amounts. Thorite is rarely found unaltered. Many of the analyses show U, Fe‴, Pb, Ca in rather small amounts. One variety has been called uranothorite. It is particularly noteworthy that Zr is not found in thorite.

*Wöhlerite family:* The minerals of this family are complex in composition and varied in crystallography. Brögger (1890) described most of these minerals in detail and has placed them in two existing groups, on the basis of rather elaborate constitutional formulae. Wöhlerite, hiortdahlite and lavenite were placed in the pyroxenes; johnstrupite and mosandrite in the epidotes. There is no indication that any of these minerals are metasilicates, and the Si:O ratio is closely 1:4. Further, in order to place these in either the epidotes or pyroxenes one must make assumptions concerning the chemical relations wholly unacceptable to the writer. The simplicity of the formulae presented here as compared with Brögger's convinces the writer that they probably more nearly express the true composition. The essential difference between the members of the wöhlerite group lies in the X component of the formula. It is seen that the chief difference (if there is any real difference) between hiortdahlite and guarinite (Zambonini and Prior, 1909) is in the presence of Ti in one and Cb in the other. Wöhlerite is a Zr, Cb equivalent of the others. Johnstrupite has essential Ce as well as some Al. Brögger (1890) indicated certain crystallographic similarities between the members of this group. Peacock (1937) has re-investigated rosenbuschite and has discussed its systematic relations.

The other minerals placed in this family are very different in composition and probably not closely related in structure to the wöhlerite group. No closer relation to any other silicates, however, is apparent, and they are placed here for comparison. Gossner and Kraus (1933, 1934) have determined the cell dimensions and cell contents of several members of the wöhlerite family.

Låvenite has the composition as shown in the classification, X=(Ca, Na); Y=(Zr, Cb, Fe, Ti, Mn). It is an example of the complex substitutions possible in the rare earth and rare element silicates, as noted in the minerals of the preceding group as well as in some others previously discussed (eudialyte, steenstrupine, catapleiite, etc.). This mineral may perhaps, on chemical grounds be considered a member of the datolite family.

*Datolite family:* The four minerals in this family are closely related in crystallographic properties; they probably have some structural relations but no serial relation is known between them. The structure of euclase has been determined, but the others have not yet been worked out. It seems unlikely that datolite is very close to euclase in its structural features since Be or Al are considerably smaller than Ca in ionic radius (Fig. 5) and one or the other must have a position equivalent to that of Ca if the two minerals are isostructural. In homolite and gadolinite the indications of isostructural relations are more favorable, but it is unlikely that these are isostructural with either of the first two mentioned minerals.

*Miscellaneous orthosilocates:* The normal orthosilicates which do not readily fit into any of the previously discussed groups are placed here.

Topaz and eulytite have been studied by means of $x$-rays, and the independent $SiO_4$ tetrahedra have been established as the important structural feature. In ilvaite some Mn is found, $Fe'':Mn''=4:1$. Since zunyite has such a high F and Cl content for an orthosilicate, there must be some doubt as to its proper place in the classification. A supposedly monoclinic modification of eulytite is known as agricolite; this is a rare and little-studied mineral.

*Subsilicates:* This subtype consists of those silicates which, as before stated, have independent $SiO_4$ tetrahedra in the structure, but all of the oxygen atoms are not in these tetrahedra. In all of the previously described types all of the oxygen atoms were in the tetrahedra so that the ratio of $Si:O \leqq 1:4$. In these subsilicates the ratios are 1:5 or less to such low silicon compounds as sapphirine where the ratio is $Si:O=2:27$. The classification logically terminates with these low silicon minerals where Si plays a decreasingly important role in the structure. In any natural classification there is no sharp break, and here the silicates merge into the titanates, the borates and the rare earth minerals. The subsilicates are properly a sub-type of the orthosilicates since the $SiO_4$ tetrahedra are independent elements of the structure.

*Aluminum subsilicate family.* The three modifications of aluminum silicate save independent tetrahedra in the structure. Mullite has a structure apparently almost identical with sillimanite (Taylor 1928), and its cell dimensions are so close that only very accurate measurement can distinguish between the two. A comparison of unit cell compositions gives the following result:

Sillimanite $Al_8Si_4O_{20}$
Mullite $Al_8(AlSi_3)O_{19\frac{1}{2}}$

The interpretation of the relation between the two minerals is due to Wyckoff, Grieg and Bowen (1926), who believe that the mullite cell is actually twice the sillimanite cell and that one oxygen atom in forty is somehow missing in the structure. There are yet several discrepancies in the full mullite story. Artificial crystals have been measured by the writer. The forms [110] and [011], based on the sillimanite axial lengths, were the only important forms noted. This, in the writer's opinion indicates that the unit cell is possibly the same as that of sillimanite, and not some multiple thereof. $X$-ray pictures taken in this laboratory of single crystals of mullite have failed to show any doubling of the cell. The chemical analyses of mullite are uniformly lower in $Al_2O_3$ than the formula given. The calculated value of 71.8% of $Al_2O_3$ is to be compared with an average found value of about 70%. On pure material, as most of the artificial samples presumably were, this discrepancy is too large. The actual composition is then somewhat nearer the sillimanite composition than the given formula indicates.

The composition of staurolite is such that it could be considered as two parts of kyanite to one part $Fe(OH)_2$. This is the structure derived for the mineral, which is a kyanite structure with interleaved layers of $Fe(OH)_2$.

*Kentrolite group:* The first two minerals in the group are orthorhombic and closely similar in their crystallographic properties. Beckelite is isometric and not closely related physically to the others. However, its structure is probably somewhat similar to that of the others, since its chemical elements are of the same sort and number as are those in the kentrolite group.

The titanium subsilicates are grouped together mainly because they presumably have independent $SiO_4$ tetrahedra and extra oxygen atoms as required for this sub-type. The writer has shown in another place (Barth and Berman 1930) that lorenzenite and ramsayite are members of a series. Molengraaffite and lamprophyllite are very close in their optical properties (Larsen and Berman 1934), and the writer is convinced that they are members of another series. Astrophyllite does not fit into the latter series according to the writer's interpretation, despite its apparent similarity in physical appearance.

*Miscellaneous subsilicates.* The minerals listed are, with one exception, (dumortierite), very rare, and their relations to other silicates are little understood because complete data are lacking. They are all low in Si, as the formulae show, and are therefore placed in this sub-type. Sapphirine is really an aluminate with some Si present. The writer believes that further data on these minerals will tend to show that some of the very complex compositions given are in error. In general, it can be said that all the minerals of this section are in need of further study.

The uranium silicate minerals are all low in silica and consequently come in this part of the classification. Uranophane and sklowdowskite are apparently closely similar in crystallographic properties as well as chemically and are possibly isostructural. Intermediate compounds are not known. Soddyite is the least siliceous of the uranium silicates and one of the least siliceous of the minerals placed in the silicates. Most of the oxygen atoms in this mineral are not associated with the Si tetrahedra.

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## Index of Species

A

Acmite 359, 389
Actinolite 359, 387
Aegirite 360
Aenigmatite 362, 395
Afwillite 360
Agricolite 401
Akermanite 361, 394
Alamosite 360, 390
Albite 355, 368
Allanite 363, 399
Alleghanyite 362
Almandite 363, 398
Alurgite 384
Amesite 379
Amphiboles 359, 387
Analcite 357, 368, 374
Anauxite 357
Andalusite 364
Andradite 363
Anemousite 356, 368
Anorthite 356, 368, 395
Anorthoclase 355
Anthophyllite 359, 387
Antigorite 357, 377, 388
Aphrosiderite 381, 382
Apophyllite 358, 378
Ardennite 364
Arduinite 357, 374
Arfvedsonite 359
Ashcroftine 357, 374
Astrophyllite 362, 395, 402
Augite 359
Axinite 364

B

Babingtonite 360, 390
Barbierite 367
Barylite 362, 395
Barysilite 361, 394
Batchelorite 357, 376
Bavalite 379
Bavenite 360
Beckelite 364, 402
Beidellite 357, 376
Bementite 358, 378
Benitoite 361, 392
Bertrandite 361, 394
Beryl 361, 392, 393
Biotite 358, 384
Bisbeeite 360
Bityite 359, 386
Brandisite 384
Brewsterite 356
Britholite 363
Brittle mica 358, 382
Brunsvigite 379
Bustamite 360, 390

C

Calcium-larsenite 362
Calcium-tourmaline 361
Canbyite 357, 376
Cancrinite 356, 369
Cappelenite 364
Carnegeite 368
Carpholite 360
Catapleiite 361, 392
Celsian 355, 367

Cenosite....360
Centrallassite....358, 378
Cerite....361
Chabazite....356, 373, 374
Chalcodite....358, 383
Chamosite....381
Chlorite....358, 377, 379, 381
Chloritoid....358, 384
Chloropal....376
Chondrodite....362, 397
Chrome-clinochlore....379
Chrysocolla....360, 392
Chrysolite....362, 396
Chrysotile....359, 388
Clinochlore....379
Clinoenstatite....359, 388
Clinohedrite....361, 394
Clinohumite....362, 397
Clinoptilolite....356, 373
Clinozoisite....363
Clintonite....358, 384
Colerainite....379
Connarite....357, 377
Cookeite....358, 386
Cordierite....357, 375
Corundophilite....379
Crestmoreite....360
Cronstedtite....380, 381
Cryophyllite....385
Cummingtonite....359, 387
Cuspidine....361, 394
Custerite....394

D

Dachiardite....357, 375
Danalite....356, 370
Danburite....362, 395
Daphnite....381
Datolite....363, 400
Davyne....356, 370
Delessite....379, 381, 382
Diabantite....381, 382
Didymolite....357, 375
Diopside....359, 388
Dioptase....362
Dipyre....370
Dravite....361
Dumortierite....364, 402

E

Edenite....359
Edingtonite....357, 374
Ekmannite....383
Elpidite....361
Enstatite....359, 388
Ephesite....358
Epichlorite....358, 382, 383
Epidesmine....356, 373
Epididymite....361
Epidote....363, 399
Epistilbite....356
Erionite....356, 373
Errite....358, 378
Euclase....364, 400
Eucolite....361, 393
Eucryptite....356, 369
Eudialyte....361, 392, 393
Eudidymite....360
Eulytite....364, 400

F

Faujasite....357, 374
Fayalite....362
Feldspar....355, 366
Ferrierite....357, 374
Ferroschallerite....358, 377
Fersmannite....364
Forsterite....362, 397
Foshagite....391
Fowlerite....360, 389
Friedelite....357, 377
Fuchsite....385

G

Gadolinite....364, 400
Gageite....362, 397
Ganomalite....361, 394
Ganophyllite....359, 386
Garnet....362, 397
Gedrite....359
Gehlenite....361, 394
Gillespite....358, 378
Gismondite....356
Glaucochroite....362, 396
Glauconite....358, 386
Glaucophane....359
Gmelinite....356, 373
Gonnardite....357, 374
Griffithite....358, 382
Grochauite....379
Grossularite....363
Grunerite....359
Guarinite....363, 400
Gyrolite....358, 378

H

Hackmanite....356
Halloysite....376
Hancockite....363, 399
Hardystonite....361, 394
Harmotome....356, 373
Harstigite....362, 395
Hastingsite....359
Hauyne....356
Hedenbergite....359, 388
Hellandite....363
Helvite....356, 370
Hemimorphite....361, 394
Heualandite....356, 373
Hillebrandite....360, 391
Hiortdahlite....363, 399
Hodgkinsonite....362, 397
Holmquistite....359
Homilite....364, 400
Hornblende....359, 387
Hortonolite....362

Humite....362, 397
Hyalophane....355, 367
Hyalotekite....360, 391
Hypersthene....359, 388

I

Ilvaite....364, 401
Indicolite....361
Inesite....360, 391
Iron-rhodonite....360, 389

J

Jadeite....360, 389
Jeffersonite....359
Johnstrupite....363, 399
Jurupaite....360, 392

K

Kaliophilite....356, 369
Kammererite....379
Kaolin....357, 376
Kasolite....364
Kearsutite....359
Kentrolite....364, 402
Klementite....382
Knebelite....362
Kornerupine....364
Kossmatite....384
Kotschubeite....379
Kyanite....364, 402

L

Labradorite....356, 368
Lamprophyllite....364, 402
Larnite....362, 396
Larsenite....362, 396
Laubanite....357, 375
Laumontite....357, 374
Låvenite....363, 399, 400
Lawsonite....362, 395
Lazurite....356
Leifite....355, 366
Lepidolite....384
Leptochlorite....358, 380
Lessingite....363
Leuchtenbergite....379
Leucite....356, 368
Leucophanite....361, 394
Leucophoenicite....362
Leucosphenite....361
Levynite....357
Lorenzenite....364, 402

M

Mackintoshite....364
Magnesium orthite....363, 399
Manandonite....386
Manganepidote....363, 399
Manganophyllite....385
Margarite....358, 383
Margarosanite....360, 390
Marialite....356, 370
Meionite....356, 370
Melanocerite....364
Melilite....361, 394
Melanotekite....364
Meliphanite....361
Merwinite....362, 396
Mesolite....357, 374
Metachlorite....379
Mica....358, 384
Microcline....355, 367
Microsommite....356, 370
Milarite....355, 366
Mizzonite....370
Molengraafite....364, 402
Molybdophyllite....361, 394
Monticellite....362
Montmorillonite....376
Mordenite....356, 372
Mosandrite....363, 400
Mullite....364, 401
Murmanite....361, 394
Muscovite....358, 384

N

Nagatelite....363, 399
Narsarsukite....359, 388
Nasonite....361
Natrolite....357, 374
Natron-catapleiite....361, 393
Nephelite....356, 368
Nepouite....357
Neptunite....360, 391
Nontronite....376
Norbergite....362, 397
Noselite....356

O

Okenite....358
Olivine....362, 396
Orthoclase....355, 367
Ottrelite....358, 383

P

Paragonite....384
Pargasite....359
Parsettensite....378
Pectolite....360, 390
Pennine....379, 382
Petalite....355, 366
Phenakite....362, 397
Phengite....384
Phillipsite....356, 373
Phlogopite....384
Pholidolite....358, 386
Piedmontite....363, 399
Pigeonite....359, 388
Plancheite....360
Pollucite....356, 368
Polylithionite....385
Prehnite....358, 383
Prochlorite....379, 381, 382
Pseudophite....381

Ptilolite.......372
Pumpellyite.......363, 399
Pycnochlorite.......379
Pyrope.......363
Pyrophyllite.......357
Pyrosmalite.......357, 377
Pyroxene.......359, 388
Pyroxenoid.......360, 389
Pyroxmangite.......360

R

Radiophyllite.......360
Ramsayite.......364, 402
Rhodonite.......360, 389, 391
Rhönite.......395
Riebeckite.......359
Rinkite.......363
Rinkolite.......363
Ripidolite.......379, 381
Riversideite.......360, 392
Roepperite.......362
Roscoelite.......384
Roseite.......358
Rosenbuschite.......363, 400
Rowlandite.......361
Rumpfite.......379

S

Sanbornite.......358, 378
Saponite.......358, 382
Sapphirine.......364
Sarcolite.......363, 398
Scapolite.......356, 370
Schallerite.......357, 377
Schefferite.......359
Schizolite.......360
Schorl.......361
Schorlomite.......398
Scolecite.......357
Searlesite.......360
Serendibite.......364
Serpentine.......377
Seybertite.......384
Shattuckite.......360
Sheridanite.......379
Siderophyllite.......384
Silica.......355, 366
Sillimanite.......364, 401
Sklowdowskite.......364, 402
Sobralite.......360, 389
Sodalite.......356, 370
Soda-melilite.......361
Soda-microline.......355
Soda-orthoclase.......355
Soddyite.......364, 402
Spessartite.......363
Spodumene.......360, 389
Staurolite.......364, 402
Steenstrupine.......361, 392
Stellerite.......356, 373
Stilbite.......356, 373
Stilpnomelane.......358, 383
Stokesite.......360
Sursassite.......399

T

Tabergite.......379
Talc.......357, 377
Taramellite.......360, 391
Tephroite.......362
Thalenite.......361, 394
Thomsonite.......357, 373
Thorite.......363, 399
Thortvietite.......361, 394
Thuringite.......382
Tinzenite.......364
Titanite.......364
Titanium garnet.......363
Topaz.......364, 400
Tourmaline.......361, 392, 393
Tremolite.......359, 387
Trimerite.......362, 397
Troostite.......362
Truscottite.......358, 378

U

Ultramarine.......370
Uranophane.......364, 402
Uranothorite.......399
Ussingite.......361
Uvarovite.......363

V

Vermiculite.......358
Vesuvianite.......363, 398
Volchonskite.......376

W

Wellsite.......356, 373
Wernerite.......370
Willemite.......362, 397
Wöhlerite.......363, 399
Wollastonite.......360, 389, 391

X

Xanthophyllite.......384
Xonotlite.......360, 391

Z

Zeolites.......356, 357, 371
Zeophyllite.......357, 377
Zinc-schefferite.......359
Zinnwaldite.......385
Zircon.......363, 399
Zoisite.......363, 399
Zunyite.......364, 401

# LEUCITE AND PSEUDOLEUCITE

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## The Pseudoleucite Problem

The lavas of the volcanic area immediately to the north of Lake Kivu in Central Africa present an interesting variety of leucite-bearing types. The leucite occurs in some examples as phenocrysts showing the characteristic form and in others as one of the minerals of the groundmass. Usually the leucite has persisted as such but in some of the lavas of Mt. Mikeno phenocrysts of that mineral are peripherally changed to pseudoleucite, an intergrowth of orthoclase and nepheline. This change in the leucite is one that has long been recognized by petrologists, and observed in rocks from a number of localities. The formation of the soda-rich mineral nepheline as one of the products of the change has raised the question of the composition of the original leucite. Knight (1906) has suggested that the leucite had a notable content of $Na_2O$ replacing $K_2O$ and that by simple breakdown of this soda-bearing variety of leucite, consequent upon falling temperature, an intergrowth of orthoclase and nepheline was formed, the supposed metasilicate solid solution thus giving rise to a polysilicate and an orthosilicate. No less an authority on leucitic rocks than our late colleague, Henry S. Washington, leaned strongly to that view.

With this question in mind it was decided that the nature of the leucite in typical examples of these rocks should be determined, not only in rocks showing phenocrysts partly changed to pseudoleucite but also in those with leucite as a groundmass mineral.

## Leucitophyre and its Leucite Phenocrysts

Among the specimens collected on Mt. Mikeno there are many of lavas carrying leucite phenocrysts. In one of these, a leucitophyre, these phenocrysts, greyish when freshly broken, have diameters up to 5 mm. and are surrounded by a white rim. There are phenocrysts of augite and of magnetite and the groundmass, which is very fine grained, contains these two minerals in considerable amounts but is largely made up of leucocratic minerals, a mixture of nepheline and soda-orthoclase without leucite. The white rims of the leucite phenocrysts are found to be made up of fibrous orthoclase intergrown with another mineral of slightly higher refringence which is presumably nepheline. The rim is therefore typical pseudoleucite.

Table 1. Analyses of Leucitic Rocks

| | I | II | III | | I(a) | I(b) | II(a) | II(b) |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 47.94 | 43.16 | 55.4 | or | 35.0 | — | 15.6 | — |
| $Al_2O_3$ | 16.24 | 13.46 | 23.3 | ab | 4.7 | 21.1 | 1.6 | 8.6 |
| $Fe_2O_3$ | 3.19 | 2.44 | 0.5 | an | 1.7 | 1.7 | 18.6 | 18.6 |
| FeO | 5.54 | 11.35 | | lc | — | 27.5 | — | 12.2 |
| MgO | 3.06 | 8.42 | 0.0 | ne | 23.0 | 14.1 | 9.7 | 5.8 |
| CaO | 7.09 | 11.08 | 1.1 | | | | | |
| $Na_2O$ | 5.71 | 2.28 | 1.8 | di | 21.4 | 21.4 | 27.3 | 27.3 |
| $K_2O$ | 5.91 | 2.65 | 18.3 | wo | 0.6 | 0.6 | — | — |
| $H_2O+$ | 0.48 | 0.13 | 0.2 | ol | — | — | 14.4 | 14.4 |
| $H_2O-$ | 0.21 | 0.03 | | mt | 4.6 | 4.6 | 3.5 | 3.5 |
| $TiO_2$ | 3.07 | 4.20 | 0.2 | il | 5.9 | 5.9 | 8.1 | 8.1 |
| $P_2O_5$ | 0.82 | 0.45 | | ap | 2.0 | 2.0 | 1.0 | 1.0 |
| Cl | 0.18 | — | | | | | | |
| MnO | 0.18 | 0.21 | | | | | | |
| | 99.62 | 99.86 | 100.8 | | | | | |

I. Leucitophyre, Mt. Mikeno, Belgian Congo. R. B. Ellestad analyst.
II. Leucite theralite, Nyamlagira volcano, Belgian Congo. A. Willman analyst.
III. Leucite out of leucite theralite II. R. B. Ellestad analyst.
I(a). Norm of I.
I(b). Alternative recalculation of I.
II(a). Norm of II.
II(b). Alternative recalculation of II.

The chemical composition of the rock is given in Table 1 together with the norm. There is no leucite in the norm, a condition which arises from the fundamental assumption underlying the calculation, whereby silica is assigned preferably to the potash-alumina silicate. Moreover there is 23 per cent nepheline in the norm. An alternative recalculation, also given in Table 1, in which all the $K_2O$ is assigned to leucite gives some 27 per cent leucite, 14 per cent nepheline and of course no orthoclase. The proportions of the modal salic constituents are intermediate between those of the norm and those of this alternative recalculation. The rock may be called leucitophyre although it is transitional towards leucitite.

The fact that the leucite is only peripherally changed to pseudoleucite suggests that the intervention of the liquid magma was necessary to the action and that the liquid contributed the soda necessary to the production of nepheline. However, this is not altogether conclusive and it is desirable that the character of the leucite phenocrysts should be determined.

In this case it was not considered necessary to analyze the leucite. Excellent material, all but free from inclusions of any kind, was obtained by picking out selected phenocrysts, and the purity of the leucite was determined by measuring the melting temperature. This can be done on a much smaller amount of material than that necessary for chemical analysis. With the aid of this unusually pure sample of the phenocrysts it was possible to prove that the leucite can contain no more than a small amount of $Na_2O$. The crystals are not pure $KAlSi_2O_6$ and therefore show a melting interval rather than a melting point, but the temperature of completion of melting was found to be 1660°, only 26° lower than that of pure $KAlSi_2O_6$. From the equilibrium diagram of the system, $KAlSiO_4$–$NaAlSiO_4$–$SiO_2$, as determined by Schairer and Bowen (1935) and given in Figure 1, it is possible to state that the leucite can contain no more than 1–1.5 per cent $Na_2O$ replacing $K_2O$.

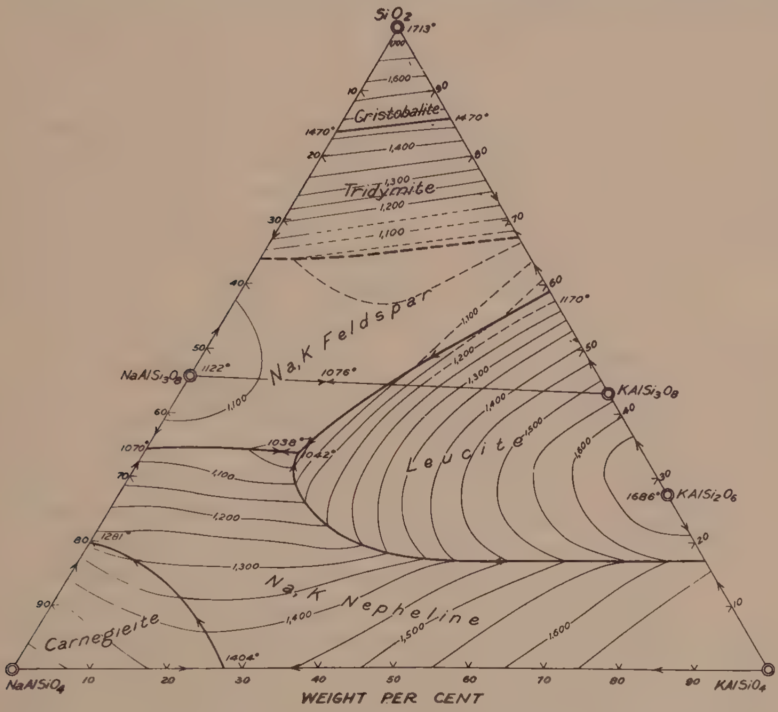

FIG. 1. Equilibrium diagram of the ternary system, $NaAlSiO_4$–$KAlSiO_4$–$SiO_2$ (after Schairer and Bowen.)

The temperature of completion of melting of a leucite having a content of $Na_2O$ corresponding with that ordinarily contained in pseudoleucite (6–7 per cent), if such a leucite exists, would be about 1350°, or some 300° lower, as shown by the same diagram.

Since the composition of this leucite is such that it could not give typical pseudoleucite by simple transformation it is necessary to suppose that reaction with liquid magma was essential. That such reaction could give the observed result is indicated by experimental results which reveal the nature of the reaction.

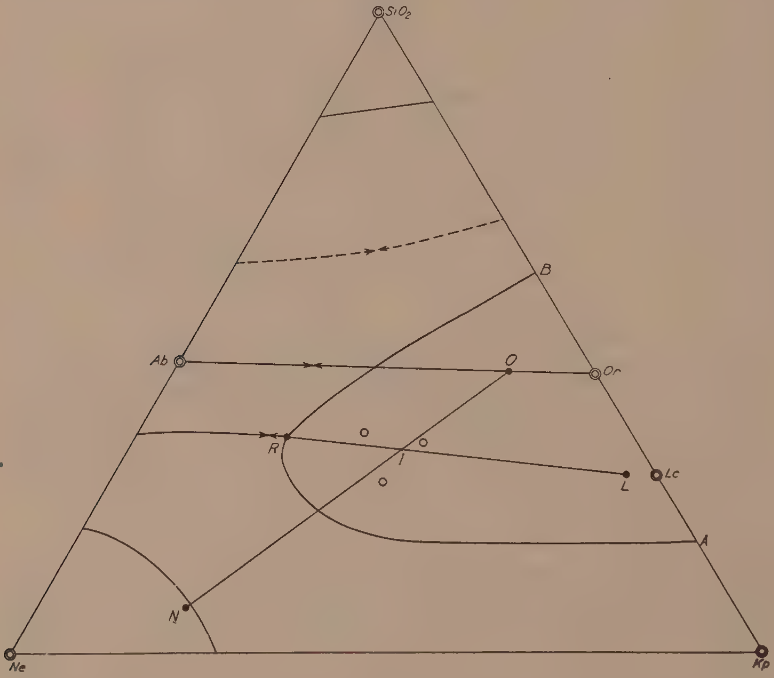

FIG. 2. Diagram to illustrate formation of pseudoleucite. Hollow circles—three analyzed pseudoleucites (neglecting minor oxides). Solid circles—composition of reacting phases.

In order to illustrate this fact we have plotted upon the ternary equilibrium diagram, Figure 2, the compositions of three analyzed pseudoleucites as given by Knight (1906). Examination of this diagram shows that if a leucite of the composition *L* (corresponding with that of the usual leucite) reacts with liquid of composition *R* (that of the pseudoleucite reaction point) it could give a solid product corresponding closely with the analyzed pseudoleucites, since their composition lies close to the line *RL*. Moreover it shows that this solid product could be made up of orthoclase of composition *O* and nepheline of composition *N*, and the line

*NO* likewise passes close to the points indicating the compositions of the analyzed pseudoleucites.

In the ideal case where all the compositions involved could be represented in the diagram of the ternary system the actual quantitative relations of the phases could be stated. Thus liquid and leucite in the proportions given by the lengths *LI* and *IR* would react to give orthoclase and nepheline in proportions corresponding to the lengths *NI* and *IO*. In other words, two parts (by weight) of liquid (*R*) react with one part leucite (*L*) to give a solid product consisting of two parts orthoclase (*O*) and one part nepheline (*N*). In order to reach these figures it has been necessary, of course, to assign definite compositions to the orthoclase, the nepheline and the leucite but the assumed compositions are probably not far from the true values. In the ternary system the composition of all these phases in equilibrium with liquid at the pseudoleucite reaction points is necessarily fixed but it has not yet been possible to determine the composition of the solid phases experimentally.

It should be pointed out that some variation in the bulk composition of pseudoleucite might be expected even if the phases concerned were all of compositions such that they could be accurately represented in the ternary diagram. The variation will arise from the fact that the cooling liquid, changing in composition by subtraction of leucite and therefore moving in the leucite field, will not ordinarily reach the boundaries of that field exactly at the point *R* but will first encounter either the curve *BR*, in which case some of the leucite will be transformed to orthoclase only, or else the curve *AR*, in which case some nepheline will be formed. The pseudoleucite as finally formed at *R* may therefore contain an excess of either orthoclase or nepheline. The composition of pseuodoleucite may show further variation in view of the fact that in the natural magmas compositions do not lie in the ternary system. It is not to be expected that pseudoleucite compositions should always coincide with the point *I*. Rather is it that there should be a tendency to cluster around that point and this there seems to be.

## GROUNDMASS LEUCITE

The considerations brought out thus far tend to show that the phenocrystic leucites which have been transformed to pseudoleucite in many rocks have probably been close to theoretical leucite in composition and not notably soda rich. At the same time it should be pointed out that the general relations in the equilibrium diagram to which repeated reference is made in this paper make it clear that phenocrystic leucites are those that are the most likely to show high $K_2O$ content, since the high temperatures lie towards the composition of the pure potash compound.

The question whether leucite notably rich in soda can form from any liquid is not decided by such considerations, nor is it decided by the experimental work, for as we have noted, little was accomplished in that work in the way of determining the exact composition of solid phases. It is still possible to suppose, therefore, that in some leucitic rocks with considerable soda content, the groundmass leucites might contain notable amounts of soda. For this reason a rock containing leucites in the groundmass has been examined in some detail, a leucite theralite from the crater of Nyamlagira being chosen.

## LEUCITE THERALITE AND ITS LEUCITE

The inner walls of the crater of the active volcano, Nyamlagira, are made up of a rock which is parted into layers a foot or somewhat less in thickness. This effect is apparently due to jointing; otherwise the rock is of very massive appearance and there is no clear evidence of separation into distinct flows. The rock is coarser in grain than the lava flows of the area and may be tentatively regarded as the remnant of a plug or neck, some of which has been removed by explosion. Similar rocks are found as bombs on the slopes of the volcano.

The rock has abundant large titanaugites, less abundant olivines and titaniferous magnetite, in a groundmass rather indefinitely marked off, since the minerals of the groundmass attain nearly the same dimensions. These minerals are principally plagioclase, pyroxene and leucite. The plagioclase is strongly zoned and passes more or less continuously, but with some oscillation, from basic bytownite to a broad outer border which has distinctly lower indices than balsam and must be in part anorthoclase. The latter mineral shares with the leucite or at least with the outer borders of leucite an interstitial relation to the other minerals. There are also some grains probably to be referred to nepheline, some magnetite, apatite and rare biotite.

The chemical composition of this leucite theralite is given in Table 1 together with the norm. There is no normative leucite, the undersilicated character of the rock finding its expression in normative nepheline, in addition to olivine. An alternative recalculation in which all the $K_2O$ is assigned to leucite, also given in Table 1, shows some 12 per cent leucite and, of course, no orthoclase. It also shows altogether too much albite. In the proportions of salic minerals the actual mode of the rock is intermediate between the norm and this alternative recalculation. An older analysis of a leucite theralite bomb from Nyamlagira is given by Finckh (1912). The analysis (by Hauser) seems to be of inferior grade. The rock is described as rich in leucite yet the norm, calculated by Washington (1917), shows only a fraction of a per cent of nepheline and no leucite.

The given value of $Fe_2O_3$ is too high and that of MgO too low, for the mineral assemblage present. Indeed the rock appears to be sensibly identical with that here described and analyzed.

The nature of the leucite is our immediate concern. It was not possible to get a clean enough separation of leucite to permit determination of its character by the melting-point method. A quantity sufficient for chemical analysis was therefore separated. Only a small sample was available, and it contained small amounts of the associated minerals, principally feldspar, nevertheless the analysis, given in Table 1, leaves no question as to the nature of the leucite. There is but 1.8 per cent $Na_2O$ altogether, and some of this is in the associated feldspar. The leucite can contain no more than the 1–1.5 per cent $Na_2O$ ordinarily found in that mineral. It is plain, then, that groundmass leucite has no notable tendency towards a higher soda content than has phenocrystic leucite, which is that usually analyzed.

These determinations upon leucites of contrasted occurrence may be accepted as showing, with little possibility of doubt, that leucite never has a high content of soda; in other words that, in leucite, potash is replaceable by soda only to a very limited degree, and that, for development of pseudoleucite, reaction with liquid magma is essential.

The broader implications of the pseudoleucite reaction have been discussed at some length elsewhere by Bowen (1928). Suffice it to say here since leucite can separate not only from undersilicated magmas but also from certain types of oversilicated magmas, and since the local accumulation and subsequent transformation by pseudoleucite reaction may give rise to a nepheline-bearing rock, we have in these relations the possibility of the development of a nepheline rock as a crystallization differentiate of an oversilicated magma.

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# THE *X*-RAY DETERMINATION OF LATTICE CONSTANTS AND AXIAL RATIOS OF CRYSTALS BELONGING TO THE OBLIQUE SYSTEMS

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## CONTENTS

Abstract . . . . . 416
Introduction . . . . . 417
Important Reciprocal Relations . . . . . 417
Relative Precision of *X*-Ray Determinations . . . . . 420
Determination of Linear Lattice Constants . . . . . 422
    General Remarks . . . . . 422
    Direct Determination of $a$, $b$, and $c$ . . . . . 422
    Direct Determination of $a^*$, $b^*$, and $c^*$ . . . . . 424
Determination of Angular Lattice Constants . . . . . 425
    Determination of $\alpha$, $\beta$, and $\gamma$ . . . . . 425
        Method of Dome Offsets . . . . . 425
            Monoclinic Case . . . . . 426
            Triclinic Case . . . . . 428
        Method of Triangulation . . . . . 431
    Direct Determination of $\alpha^*$, $\beta^*$, and $\gamma^*$ . . . . . 431
        Method of $\omega$ Separations . . . . . 431
        Method of Triangulation . . . . . 431
The Determination of All Lattice Constants from One Crystal Setting . . . . . 432
Optimum Procedure Leading to Maximum Accuracy in Lattice Constants . . . . . 433

## ABSTRACT

The determination of all the lattice constants of crystals belonging to the oblique systems has never received a systematic discussion, as a consequence of which the relative precisions of the several possible methods have not been treated, and certain possible methods have been neglected. A brief systematic discussion of the subject is given here. A distinction is made between determinations based upon chart measurements and those based upon steel scale and vernier measurements. The following new developments are included: (a) The attainment of precision in the determination of linear lattice constants with the rotating crystal technique. (b) The attainment of relative precision in the determination of angular lattice constants by the method of dome offsets. (c) The attainment of high precision in the determination of angular lattice constants by the method of triangulation.

The problem of the determination of all lattice constants with one crystal setting is discussed. This can be solved by Weissenberg methods without any plotting, with a precision comparable to that of optical goniometry. The determination of all lattice constants with extreme precision is also briefly considered, and it is shown that if the crystal can be oriented in three noncoplanar zones, these may be determined to about six significant figures, or with interaxial angles accurate to a few seconds of arc. The precision is independent of minor orientation errors and independent of minor crystal imperfections.

## INTRODUCTION

The science of geometrical crystallography is primarily concerned with the study of the three-dimensional patterns of the repetitions of atoms in crystals. The motifs (the atom clusters themselves) repeated by the patterns are of no concern in this connection.

The sciences of descriptive geometrical crystallography, geometrical crystal classification, and geometrical crystal identification are based upon the possibility determinating the characteristic three-dimensional patterns of crystals. Patterns have two determinable fundamental aspects:

(a) A qualitative aspect—the determination of the pattern type. In crystals, this corresponds with the determination of the point-group symmetry (crystal class), the space lattice type, and the space group.

(b) A quantitative aspect—The determination of the magnitudes of the geometrical constants of the repeat periods. In crystals, this corresponds with a determination of the space lattice cell lengths, $a$, $b$, $c$, and interlinear angles, $\alpha$, $\beta$, and $\gamma$.

The Weissenberg method (assisted by the simple rotating crystal method) is ideally suited to making both of these kinds of determinations.

The use of the Weissenberg method in the determination of the qualitative aspects (a) of the pattern has already been treated by the writer (1934, 1935, 1936A). The determination (b) of the lattice constants of crystals belonging to the orthogonal systems is relatively simple, and the methods are well known except in their precision aspects (Buerger, in press). The methods of arriving at the axial elements of crystals belonging to the oblique systems have received no systematic attention but have appeared from time to time in the form of incidental papers, appendanges and notes by Halla (1932, pp. 321–323), Tunell (1933), Barth & Tunnel (1933), Crowfoot (1935, pp. 218–222), Buerger (1936B, p. 580). As a result of this sporadic attention the comparative precisions of the several methods have been neglected, and several possible methods of determining important lattice elements have been overlooked. A brief systematic account of the determination of important linear and angular lattice constants of crystals belonging to the two oblique systems (monoclinic and triclinic) is given here.

## IMPORTANT RECIPROCAL RELATIONS

Since each spot on a Weissenberg photograph corresponds with a point of the reciprocal lattice (Buerger, 1934, p. 357), many of the possible measurements made on a Weissenberg photograph have an immediate meaning in reciprocal space. Some of them, however, have an important meaning in direct space.

If the customary symbols,

| | axial lengths | inter-axial angles | volume |
|---|---|---|---|
| direct lattice | $a,\ b,\ c$ | $\alpha,\ \beta,\ \gamma$ | $v$ |
| reciprocal lattice | $a^*,\ b^*,\ c^*$ | $\alpha^*,\ \beta^*,\ \gamma^*$ | $v^*$ |

are adopted, then the important relations between direct and reciprocal lattice are as follows:

direct from reciprocal,

$$a=\frac{b^*c^* \sin \alpha^*}{v^*} \tag{1}$$

$$b=\frac{a^*c^* \sin \beta^*}{v^*} \tag{2}$$

$$c=\frac{a^*b^* \sin \gamma^*}{v^*} \tag{3}$$

reciprocal from direct,

$$a^*=\frac{bc \sin \alpha}{v} \tag{4}$$

$$b^*=\frac{ac \sin \beta}{v} \tag{5}$$

$$c^*=\frac{ab \sin \gamma}{v}. \tag{6}$$

The volume, $v$, of a triclinic parallelopiped may be expressed (Kraus & Mez, 1901, p. 390):

$$v=abc \sin \alpha \sin \beta \sin \gamma^* \tag{7}$$

$$=abc \sin \alpha \sin \beta^* \sin \gamma \tag{8}$$

$$=abc \sin \alpha^* \sin \beta \sin \gamma \tag{9}$$

$$v^*=a^*b^*c^* \sin \alpha^* \sin \beta^* \sin \gamma \tag{10}$$

$$=a^*b^*c^* \sin \alpha^* \sin \beta \sin \gamma^* \tag{11}$$

$$=a^*b^*c^* \sin \alpha \sin \beta^* \sin \gamma^*. \tag{12}$$

The volumes of the two cells are also reciprocal:

$$v=\frac{1}{v^*}. \tag{13}$$

Substitituting (7)–(12) in (1)–(6) gives the important relations:

$$a=\frac{1}{a^* \sin\beta^* \sin\gamma}=\frac{1}{a^* \sin\beta \sin\gamma^*} \tag{14}$$

$$b=\frac{1}{b^* \sin\gamma^* \sin\alpha}=\frac{1}{b^* \sin\gamma \sin\alpha^*} \tag{15}$$

$$c=\frac{1}{c^* \sin\alpha^* \sin\beta}=\frac{1}{c^* \sin\alpha \sin\beta^*} \tag{16}$$

$$a^*=\frac{1}{a \sin\beta \sin\gamma^*}=\frac{1}{a \sin\beta^* \sin\gamma} \tag{17}$$

$$b^*=\frac{1}{b \sin\alpha \sin\gamma^*}=\frac{1}{b \sin\alpha^* \sin\gamma} \tag{18}$$

$$c^*=\frac{1}{c \sin\alpha \sin\beta^*}=\frac{1}{c \sin\alpha^* \sin\beta}. \tag{19}$$

The polarform relation of Goldschmidt (1886, p. 14) also connects the direct and the reciprocal lattice:

$$a:b:c=\frac{\sin\alpha^*}{a^*}:\frac{\sin\beta^*}{b^*}:\frac{\sin\gamma^*}{c^*} \tag{20}$$

$$a^*:b^*:c^*=\frac{\sin\alpha}{a}:\frac{\sin\beta}{b}:\frac{\sin\gamma}{c}. \tag{21}$$

Goldschmidt's polarform relation, unfortunately, is of no use in the initial stages of a calculation, because solution of it for a direct lattice element from a reciprocal element, for example, requires a previous knowledge of one of the other two corresponding direct elements.

The direct and reciprocal angles are related to one another independent of the linear elements:

$$\alpha=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\alpha^*\right)}{\sin\beta^*\sin\gamma^*}} \tag{22}$$

$$\beta=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\beta^*\right)}{\sin\alpha^*\sin\gamma^*}} \tag{23}$$

$$\gamma=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma^*}{2}\right)\sin\left(\frac{\Sigma^*}{2}-\gamma^*\right)}{\sin\alpha^*\sin\beta^*}} \tag{24}$$

$$\alpha^*=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\alpha\right)}{\sin\beta\sin\gamma}} \tag{25}$$

$$\beta^*=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\beta\right)}{\sin\alpha\sin\gamma}} \tag{26}$$

$$\gamma^*=2\sin^{-1}\sqrt{\frac{\sin\left(\frac{\Sigma}{2}\right)\sin\left(\frac{\Sigma}{2}-\gamma\right)}{\sin\alpha\sin\beta}}. \tag{27}$$

## THE RELATIVE PRECISION OF *X*-RAY DETERMINATIONS

The Weissenberg film is a two dimensional sheet and consequently two coördinates completely specify one of its points. The position of a reflection on the film is fixed in space while the film is a cylindrical surface in the camera, by two coplanar angles: $\phi$, the reflection angle, and $\omega$, the azimuthal orientation of the crystal at the time of reflection. The actual corresponding measurements made on the film to determine these are linear ones, and designated $x$ and $\eta$ respectively (Fig. 1). Now, from the point of view of precision, it is important to observe that the original equatorial reflections are focussed with respect to the circumference of the camera but not with respect to the axis of the camera. Unless a tiny crystal is used, therefore, each reflection on an equatorial photograph will be narrow along the $x(\phi)$ axis, but drawn out normal to the $\eta(\omega)$ axis. Determinations of the former may therefore be accurately made, while determinations of the latter cannot. The corresponding relations for $n$-layer photographs are somewhat more complicated.

Another source of error inherent in $x$-ray determinations depends upon the fact that while $x$ coördinates are ordinarily rather reliable due to focussing, they cannot be depended upon for small values of $x$. This is because the absorption and thickness of the specimen tend to shift the center of the spot (Hadding, 1921) to a higher value of $x$. While this effect is a continuous function of $x$, the displacement is most important for spots near the center line of the film.

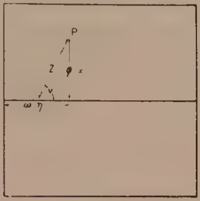

FIG. 1

A third source of error is due to the initial error in orienting the axis of the crystal parallel with the rotation axis. This sort of an error leads to only a negligible error in the $x$ coördinate of a reflection, but causes an important error in $\eta$ of approximately

$$\Delta\eta_{\max} = r \tan(2e) \tag{28}$$

were $e$ = the original angular orientation error. The resulting error in calculated $\omega$ angles thus amounts to

$$\Delta\omega_{\max} = \frac{\Delta\eta_{\max}}{K} = \frac{r \tan(2e)}{K} \tag{29}$$

where $K$ = the coupling constant of the instrument, i.e., the number of millimeters translation of the camera per degree of crystal rotation. This error is serious. It can be reduced to some extent experimentally by using a narrow layer line screen slit (which will prevent recording if the orientation error, $e$, is high) and also by increasing the coupling constant, $K$. There is a physical limit to $K$ if one wishes to keep the size of the Weissenberg instrument down to practical size.

Because of the first and last sources of error discussed, truly precise determinations of crystallographic constants cannot be based upon any methods involving measurements of $\eta$, but can only be based upon methods involving the measurement of $x$ only. In other words, any precision determinations of lattice constants must be based upon measurements of reciprocal cell translations, which correspond with direct cell interplanar spacings.

In most cases the measurements mentioned above can be made against a steel millimeter scale (Tunell, 1933, p. 183; Buerger, *in press*, fig. 9) or with a vernier caliper.[1] If measurements are made with the aid of charts, however, such as $d$-charts, $Z$-charts, or $\xi$-charts, several additional sources of inaccuracy appear. In the first place, inaccuracies in the charts themselves reduce the precision of the measurement. Second, since non-uniform scales are inherent in charts, a vernier cannot be used in subdividing the chart graduations. The use of charts therefore reduces the precision of the results still further and determinations based upon chart measurements can only be considered rough determinations.

## DETERMINATION OF LINEAR LATTICE CONSTANTS

### *General Remarks*

The linear lattice constants of crystals may be derived by making measurements leading either directly to $a$, $b$ and $c$ or by making measurements leading directly to $a^*$, $b^*$ and $c^*$. The latter scheme, at present the most accurate, is extremely tedious and roundabout for the oblique systems, since the final desired result (the direct lattice constants) can only be derived after a further knowledge of the angular lattice constants is gained (see equations (14)–(16)). If the latter can be only inaccurately determined, the calculated linear lattice constants must also remain inaccurately known.

### *Direct Determination of a, b, and c.*

It is well known that the layer line spacings of a rotating crystal photograph lead directly to the identity period of the axis of rotation. The measurement method ordinarily employed for this purpose consists of (or is the equivalent of) laying the film directly on a Bernal (1926) chart which has been reduced to scale for the camera diameter used, and reading off the $\zeta$ coördinates of the layer lines directly. The identity period along the rotation axis is then

$$T=\frac{n\lambda}{\zeta} \qquad (30)$$

$n$ = layer number

$\lambda$ = $x$-ray wavelength

$\zeta$ = reciprocal lattice coördinate of the layer line as read on the Bernal chart.

This method leads to very inaccurate estimates of the crystallographic axes because,

(a) charts are used, a source of inaccuracy previously discussed,
(b) the reflections are, in general, unfocussed normal to the $\zeta$ film coördinate,
(c) the apparent $\zeta$ coördinate increases as $\zeta$ decreases, due to absorption and thickness of the specimen, as already discussed, and
(d) orientation inaccuracies result in multiple, or broadened, layer lines.

This method can be made to yield greatly more accurate values of the identity period sought by eliminating or minimizing inaccuracies (a), (b), (c) and (d) in several ways:

(I) Inaccuracy source (a) can be eliminated by the direct measurement of the Bernal coördinate, $y$, instead of $\zeta$. This enables one to use a scale and vernier. Suitable instruments for this purpose are indicated elsewhere. The appropriate relation corresponding to (30) for computation purposes is then

$$T=\frac{n\lambda}{\sin\ \tan^{-1}\left(\frac{y}{r}\right)} \tag{31}$$

where $y$ = the height of the $n$th layer line measured from the zero layer line
$r$ = the radius of the camera

(II) Inaccuracy source (c) may be minimized by measuring only spots of large $x$ coördinates.

(III) Inaccuracy source (d) may be minimized, if recognized, by the following means: Each plane reflects to four spots on a rotation film, the spots having coördinates $x, y; x, -y; -x, y; -x, -y$. If an orientation error exists, the $y$ coördinates of the first two and the second two pairs of spots will be displaced in the same direction by approximately the same amounts. If, therefore, the difference between the $+y$ and $-y$ coördinates of these spot pairs is measured, half of this difference is nearly the correct value of $y$ to substitute in (31). If the form whose reflection is under consideration contains more than one centrosymmetrical pair of planes, as it does in the monoclinic system (but not in the triclinic system), then each of the spots in the above $+y$, $-y$ pair will be doubled. The upward shifted pair and the downward shifted pair should be considered separately for this measurement method.

This method can be carried out with the usual rotation photograph, provided the camera not only has a high $x$ ($\xi$) range, but also provided that the film lies accurately along the camera circumference in this region. More appropriate photographs for this purpose, however, may be made by a back reflection method, since in this type of photograph the $\xi$ range then becomes the maximum possible. Such photographs are required for the increase in accuracy due to focussing, next mentioned:

(IV) Focussing in the $y$ direction may be realized along the line $\xi=$a maximum, i.e., along the line $x=\pi r$. This line is unattainable in ordinary rotation films because the film ends are placed in this region. If a back reflection photograph is used, however, this region is in the middle of the film.

Ordinarily, spots will not fortuitously appear having exactly the $x$ coördinates of this line. If the rough value of the identity period, $t$, is known, however, polychromatic radiation may be employed (as from an alloy target, for example) and multiple layer lines may be produced. Spots having $x$ fortuitously on or very near this line will then have their $y$ coördinates focussed, and accurate values of $y$ may be obtained. It should be observed that the geometrical aspects of this back reflection method are analogous to the flat-film, back reflection powder method of Sachs & Weerts (1930). Therefore, further accuracy is attainable by plotting the values of the lattice constant so obtained from several layer lines, against Sachs and Weerts' function

$$\text{ctg}\,\theta\cdot\sin 4\theta. \tag{32}$$

Extrapolation of the graph to $\theta=90°$ gives a refined value of the identity period.

### *Direct Determination of a*, b*, and c**

Rough determinations of the linear reciprocal lattice constants may be made with the aid of the $Z$ scale using the relation

$$a^*,\ b^*,\ c^*=\frac{Z}{n\lambda}\cdot \tag{33A}$$

A more exact determination of these constants is identical with an exact determination of the interplanar spacings $d_{(100)}$, $d_{(010)}$, and $d_{(001)}$. This is easily accomplished from Weissenberg photographs (Buerger, 1935, p. 281) by measurements of the $x$ coördinates of the appropriate reflections. The computation in this case is

$$d=\frac{n\lambda}{2\sin\left(\frac{x}{2}\cdot\frac{360}{2\pi r_F}\right)}\cdot \tag{33B}$$

The precision of $d$ can be greatly increased with the aid of an extrapolation method developed by Bradley and Jay (1932). In this method the values of $d$ as computed from measurements of different spots of different reflection order, $n$, are plotted against $\cos^2\theta$. The extrapolation of the curve (which is a straight line for high values of $\theta$) so obtained, to $\theta = 90°$ leads to the correct value of $d$. From this the correct value of $a^*$, $b^*$, or $c^*$ can be obtained by taking the reciprocal of the appropriate multiple of $d$.

This important method of attaining precision in $a^*$, $b^*$ and $c^*$ is of the greatest value in attaining maximum precision in other crystallographic constants. A complete treatment of the subject will appear elsewhere (Buerger, *in press*).

## DETERMINATION OF ANGULAR LATTICE CONSTANTS

### *Determination of $\alpha$, $\beta$ and $\gamma$*

**Method of Dome Offsets.** The $n$-layer reflections from the orthodomes of monoclinic crystals, and from macrodomes, brachydomes, and prisms of triclinic crystals, correspond with non-central reciprocal lattice lines (Buerger, 1934, p. 375). The amount of offset or departure, $d$, from a central lattice line can be measured in the equi-inclination method with the aid of an equi-inclination lattice line template. This offset, $d$, is a function of the reciprocal lattice level height, $\zeta$, and the direct lattice angle $\alpha$, $\beta$, or $\gamma$, as graphically shown in Figs. 2 and 4. From these figures it is evident that in either the monoclinic or triclinic system, the angular offset of the $n$th reciprocal lattice line of points is the direct crystallographic angle $\beta$. A measure of $\beta$ may evidently be obtained with the aid of the following relation:

$$\tan \beta = \frac{\zeta}{d}. \qquad (34)$$

For chart determinations, $\zeta$ may be derived from the rotation photograph with the aid of the Bernal chart, and $d$ may be derived from the $n$ layer Weissenberg film by fitting the $d$ interval template over the film and reading $d/\cos\mu$ directly from the template. This method of assigning values to oblique angles has been suggested by Miss Crowfoot (1935, p. 220).

A great gain in accuracy may be obtained in this method by avoiding the use of the chart and substituting a steel scale measurement of $d$. Because of symmetry, a direct measure of $d$ may be obtained in the monoclinic system by measuring the $x$ coördinate of the orthodome reflection nearest the center of the film (Fig. 3). If $x_d$ is the cördinate of 011, then

$$d = 2 \cos \mu \sin \left( \frac{x_d}{2} \cdot \frac{360}{2\pi r} \right). \tag{34A}$$

This method is not of general application and cannot be applied in the triclinic system where symmetry is lacking. A still better way of determining *d*, however, is through the angular lag in the reflection of the dome series behind the pinacoid series, due to *d*. This angular lag, $\psi$, is a very sensitive measure of *d* for reciprocal lattice points near the origin, i.e., for dome reflections near the center of the film. The strategy of determinating *d* varies in monoclinic and triclinic cases.

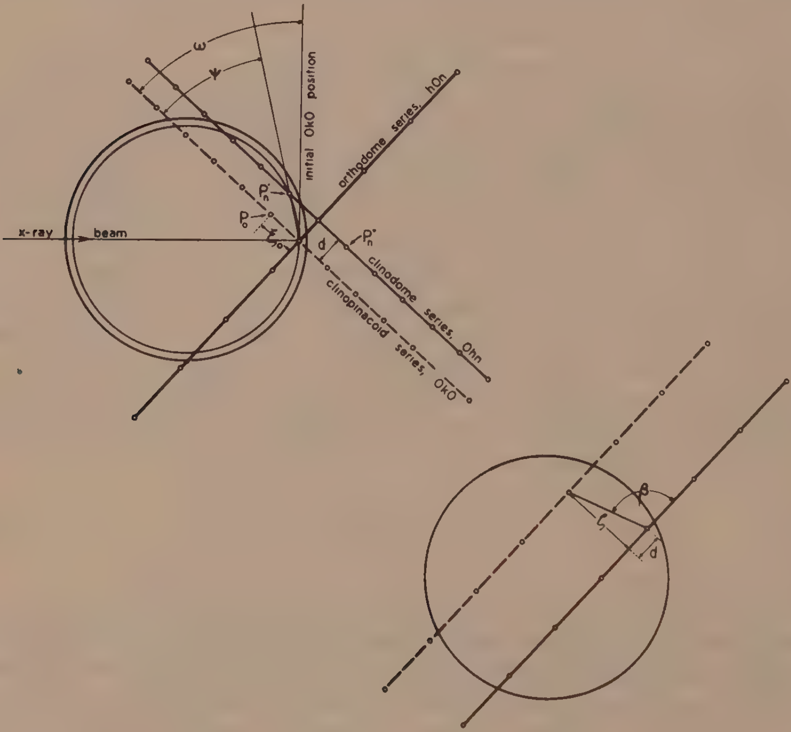

FIG. 2

*Monoclinic Case.* The following discussion applies to a monoclinic crystal rotated about the *c*-axis, but by interchange of notation, applies also to rotation about the *a*-axis. The upper part of Fig. 2 shows the important aspects of the plan of the first (or any *n*-) level of the reciprocal lattice. The beaded lines are the orthodome and clinodome series of reciprocal lattice points on this level. The latter is displaced a distance,

$d$, behind the corresponding clinopinacoid line (dashed) on the zero level; consequently a lattice point, $P_n'$, of radial coördinate $\xi_n$ from the rotation axis, reflects later than an imaginary lattice point of the same $\xi_n$ coördinate on the zero level. The amount of this angular lag, $\psi$, is given by

$$\tan\psi = \frac{d}{\xi_0} \tag{35}$$

where $\xi_0$ is the radial coördinate of $P_0$, the pinacoid reflection on the zero level corresponding with dome reflection, $P_n'$, on the $n$th level. Combining (35) with (34) gives

$$\beta = \tan^{-1}\frac{\zeta}{\xi_0 \tan\psi}. \tag{36}$$

Now the point, $P_n$, occurs in pairs symmetrically located on each side of the clinodome series. If the film coördinates of these two reflections are $\eta'$ and $\eta''$ (Fig. 3), then the distance between these spots on the film

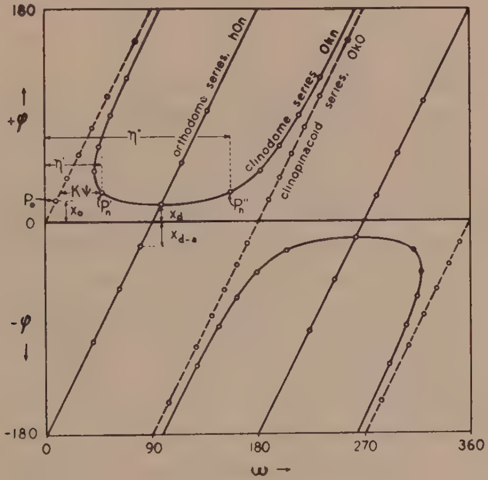

FIG. 3

$\eta''-\eta'$, is the film representation of the angular distance between these lattice points

$$\eta''-\eta' = K(180-2\psi) \tag{37}$$

or

$$\psi = 90 - \frac{\eta''-\eta'}{2K}. \tag{38}$$

Combining (36) with (38) gives

$$\beta=\tan^{-1}\left(\frac{\zeta}{\xi_0}\tan\frac{\eta''-\eta'}{2K}\right). \tag{39}$$

In this equation, $\zeta$, the reciprocal lattice layer height, is determined from the rotation photograph and may have a value refined as demonstrated on page 424, and $\xi_0$ has a value determined from the $x$ coördinate of the spot $P_0'$ on the zero layer with the aid of the relation given by Buerger (1934, p. 362, equations 10 or 11).

$$\xi_0=2\sin\left(\frac{x}{2}\cdot\frac{360}{2\pi r}\right). \tag{40}$$

A considerably more accurate estimate of $\xi_0$ may be had, however, by computing spacing, $d_{(010)}$, from a number of $\xi_0$ measurements of the $(0k0)$ series, and determining a refined value of $d_{(010)}$ by the method of Bradley and Jay (1932). $\xi_0$ is derived by the reciprocal relation:

$$\xi_0=\frac{\lambda}{d_{(0k0)}}. \tag{41}$$

Returning to equation (39), it may be said that, of the variables indicated there, $\xi_0$ can be determined with relatively great precision. $\zeta$ can also be determined with considerable precision by the methods outlined on page 424. The angular difference represented by $\eta''-\eta'$ is subject to the main lack of precision. This includes the matters mentioned on page 421, as well as the error of setting the equi-inclination angle (Buerger, 1936, p. 96). An error in this setting, however, can be detected, if present, by a lack of straightness of the orthodome series of reflections.

*Triclinic case.* In Figs. 4 and 5 the triclinic case corresponding with the monoclinic case of Figs. 2 and 3 is shown. The triclinic case offers a more complicated situation and the lack of specialization makes new measurement strategies necessary.

The value of $\xi_0$ can no longer be used in computing $d$. Instead, the relation

$$\sin\psi=\frac{d}{\xi_n} \tag{42}$$

must be used. Furthermore, the reflection $P_n$ no longer has a symmetrical companion, so some other method must be devised for the measurement of the film equivalent of $\psi$. The difficulty here is that there is no zero on the $n$ layer film from which to measure $\psi$ intervals. The difficulty can

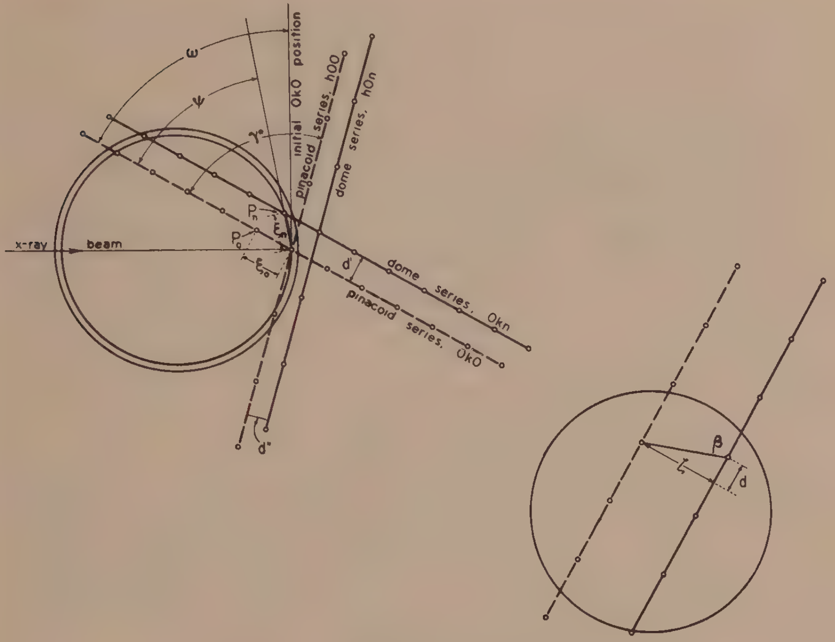

Fig. 4

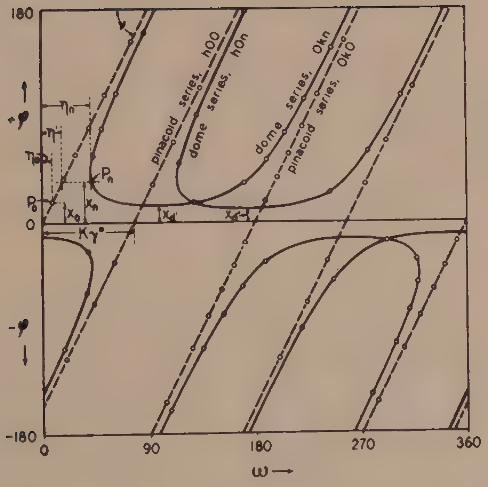

Fig. 5

be overcome if some equivalent fiducial mark can be made both on the zero and *n* layer films. This can be accomplished in either of two ways:

(a) The direct beam may be recorded on each film when the crystal rotation spindle has identical settings. The fiducial mark of the *n* layer film is then at $-2s$ compared with that on the equator film, where $s$ is given by (43) below. This method requires a very accurate crystal rotation spindle setting, which is not very easily accomplished, and also records the fiducial mark in the form of a shadow, instead of a reflection.

(b) The recommended method is to record both zero and $n$-layer on the same film without any experimental changes except the change in equi-inclination setting, and the corresponding changes in camera settings (Buerger, 1936, p. 94).

The latter change must be exact for this purpose, and is possible with the instrument designed by the writer (1936). If the camera is set on its carriage with the camera scale reading zero for the zero layer, the setting, $s$, for the $n$th layer is

$$s = r_F \tan\beta \tag{43}$$

where $r_F$ = the effective film radius

$\beta$ = the equi-inclination setting

With the zero and $n$ layers recorded on the same film, the angle of lag, $\psi$, of the dome reflections behind the pinacoid reflections can be measured (Fig. 5). For a definite reference point in the pinacoid reflection line, select a pinacoid reflection preferably with an $x$ coördinate near to the corresponding coördinate of the dome reflection $P_n$. If now, the coördinates of the several important points on the film are:

$\eta_n$, $x_n$ = the film coördinates of the dome reflection $P_n$

$\eta_0$, $x_0$ = the film coördinates of a pinacoid reflection $P_0$

$\eta'$, $x_n$ = the film coördinates of a point on the $P_0$ reflection series

then, $$K\psi = (\eta_n - \eta_0) - (\eta' - \eta_0) \tag{44}$$

and since $\tan\nu = \dfrac{x}{\eta}$, (Buerger, 1934, p. 366), (45)

$$K\psi = (\eta_n - \eta_0) - \frac{(x_n - x_0)}{\tan\nu}. \tag{46}$$

Substituting (46) in (42) gives:

$$d = \xi_n \sin\left\{\frac{1}{K}\left[(\eta_n - \eta_0) - \frac{(x_n - x_0)}{\tan\nu}\right]\right\}. \tag{47}$$

In the triclinic case, $\beta$ (or $\alpha$, by using the second set of dome offsets) is determinable by (34). The value of $d$ may be crudely obtained for this equation by fitting the equi-inclination chart to the spots on the film. It may be obtained much more accurately directly from steel scale and vernier film measurements by combining (47) and (34) which gives:

$$\beta=\tan^{-1}\frac{\zeta}{\xi_n \sin\left\{\frac{1}{K}\left[(\eta_n-\eta_0)-\frac{(x_n-x_0)}{\tan\nu}\right]\right\}}. \tag{48}$$

The sources of error in the solution of (48) are similar to those encountered in the monoclinic case, and there are two additional sources of possible inaccuracy: a possible inaccuracy in the camera setting, $s$, for the $n$th layer, and the inferior accuracy of the determination of $\xi_n$ as compared with $\xi_0$.

**Method of triangulation.** The identity periods of a crystal along $a$, $c$, and [101] may be obtained from rotation photographs about these three directions. These three identity periods form a triangle whose obtuse angle is the crystallographic angle $\beta$. Since the three sides of the triangle are known, the angle may be calculated. All three angles of a triclinic crystal may be calculated from a knowledge of the six identity periods $a$, [110], $b$, [011], $c$, and [101], and these data may be obtained from the six corresponding rotation photographs.

This method of calculating interaxial angles is not ordinarily of much practical importance since, if the crystal is sufficiently well developed to permit orientations of the rotation axes parallel with these zones, the reciprocal interaxial angles may be measured with an optical goniometer and the direct interaxial angles calculated from them.

### *Direct Determination of $\alpha^*$, $\beta^*$, and $\gamma^*$*

**Method of $\omega$ separations.** If the $b$ axis zero layer Weissenberg film is placed on the coördinate measuring device so that the measuring line is parallel with the $Z$ lines of reflection orders, then the film measurement between the reflection orders of (100) and (001) is

$$m=K\beta^* \sin\nu. \tag{49}$$

The easiest method of arriving at any crystallographic angle is thus this measurement of interplanar angles on equatorial Weissenberg films. Unfortunately it is also quite inaccurate for reasons stated on page 424.

**Method of triangulation.** The reciprocal lattice vectors $a^*$, $c^*$, $[10\bar{1}]^*$ form a triangle which includes the reciprocal lattice angle $\beta^*$. These three linear elements may be very accurately determined, hence $\beta^*$ can be very accurately computed. Similarly $\alpha^*$ can be computed from $b^*$, $c^*$, $[0\bar{1}1]^*$, and $\gamma^*$ can be very accurately computed from $a^*$, $b^*$, $[1\bar{1}0]^*$. This method is the most accurate one for determining any crystallographic angles because the angles depend upon spacing measurements, which can be very accurately made.

### THE DETERMINATION OF ALL LATTICE CONSTANTS FROM ONE CRYSTAL SETTING

An important problem which occasionally arises is the determination of all the lattice constants of a crystal which is only sufficiently well developed to permit orientation about one zone. A small acicular crystal without terminations presents a case in point. This problem cannot be solved by optical goniometric methods.

Barth and Tunell (1933) have discussed the graphical solution of this problem using the normal beam technique, and as applied to the determination of the lattice constants of chalcanthite. The problem may be more accurately solved without any plotting whatever using the equi-inclination technique, and making only steel scale and vernier measurements. Three films are required: a rotation photograph, a Weissenberg equator photograph, and an equi-inclination Weissenberg *n*-layer photograph. If the symmetry of the latter proves the crystal to be triclinic, it is desirable, for maximum accuracy, to have, in addition, another single film combining the equator and equi-inclination Weissenberg *n*-layer recording.

Suppose that the crystal is undescribed. The needle axis (or zone sufficiently well developed for orientation) may be chosen as the *c*-axis. The status of information determinable from the photographs is then as follows:

Computable from film measurements discussed: $a^*$, $b^*$, $c$, $\alpha$, $\beta$, $\gamma^*$
Remaining direct lattice constants to be found: $a$, $b$, $\gamma$

Of the remaining direct lattice elements, $a$ may be computed from the upper list with the aid of (14) and $b$ with the aid of (15). With these direct elements known, $\gamma$ may be computed from Goldschmidt's polar-form relation (21). The appropriate equations to use for the computation of the several lattice constants for different rotation axes is indicated in table 1.

It follows from the above discussion that a single setting of a crystal permits the preparation of *x*-ray films from which all lattice constants can be computed. No graphical interpretation or construction is required, and the results have an accuracy comparable with those obtainable from surface morphological studies of a well developed crystal made with an optical goniometer, provided the precautions discussed above are observed. The results are distinctly inferior to those obtained by optical goniometry if chart measurements are used for computations.

## OPTIMUM PROCEDURE LEADING TO MAXIMUM ACCURACY IN LATTICE CONSTANTS

It has been pointed out that measurements of $\eta$ ($\omega$) are subject to maximum errors and that therefore computations based upon these measurements are least reliable, while measurements of $x$ ($\phi$) are made with great accuracy. Add to this the fact that the latter measurements are transposable without error into interplanar spacing values, $d_{(kkl)}$, which can be refined by Bradley and Jay's method, and it is apparent that crystal lattice constants which can be expressed as functions of $x$ measurements alone can be determined with the greatest precision.

Now, all lattice constants can be expressed in terms of such measurements, provided only that a crystal is available which is sufficiently well developed to permit orientations for rotations about any three noncoplanar axes. Suppose that these axes are chosen as the three crystallographic axes. Then, with the aid of three equatorial Weissenberg photographs, the data given in column II below can be directly determined.

| I | II | III |
|---|---|---|
| rotation axis | precisely determinable constants | additional contants precisely computable from values in column II |
| $a$ | $b^*$, $[01\bar{1}]^*$, $c^*$ | $\alpha^*$ |
| $b$ | $a^*$, $[10\bar{1}]^*$, $c^*$ | $\beta^*$ |
| $c$ | $b^*$, $[1\bar{1}0]^*$, $a^*$ | $\gamma^*$ |

From the six distinct linear reciprocal values in column II, the reciprocal lattice angles in column III can be precisely computed by the method of triangulation. From these reciprocal angles, the direct lattice angles may be computed with the aid of (22), (23), and (24). With the values of $a^*$, $b^*$, $c^*$; $\alpha^*$, $\beta^*$, $\gamma^*$; $\alpha$, $\beta$, and $\gamma$, which are then available, the values of $a$, $b$, and $c$ may be precisely computed with the aids of equations (14), (15) and (16).

All these values rest solely upon refined spacing measurements. The results are easily comparable, if not superior, to those computed from interfacial angle measurements made with an optical goniometer, and this accuracy is obtainable without much precaution. The method is of such obvious promise that the writer (1936 C) has developed a special back-reflection Weissenberg instrument for taking full advantage of it.

The instrument, and method of attaining extreme precision in the determination of all lattice constants with its aid, will be described elsewhere (Buerger, *in press*). It may be mentioned that, by the methods there outlined, linear lattice constants can be determined with a precision of about six significant figures (Axial ratios are now customarily quoted to four significant figures.) Since this precision pervades the entire work, the angular lattice constants can be determined with an accuracy of a few seconds of arc. This represents a great improvement in crystal goniometry, and it may be mentioned that the method is almost independent of crystal imperfections which, in ordinary optical goniometric work, prevent the attainment of even the angular measuring accuracy possible in the instrument.

TABLE 1. TABULATION OF COMPUTATIONAL FORMULAE NECESSARY IN THE DETERMINATION OF ALL LATTICE CONSTANTS FROM ONE CRYSTAL SETTING. *M*, CORRECT FORMULA FOR MONOCLINIC CRYSTAL; *T*, FOR TRICLINIC CRYSTAL.

| I rotation axis | II constants directly computable | III formula for rough computation from chart measurements | IV formula for accurate computation from steel scale measurements | V constants indirectly computable | VI formula for computation of values of V from values of II |
|---|---|---|---|---|---|
| $a$ | $a$ | (30) | (31) | | |
| | $b^*$ | (33A) | (33B) | $b$ | (15) |
| | $c^*$ | (33A) | (33B) | $c$ | (16) |
| | $\alpha^*$ | (49) | triangulation | $\alpha$ | (21) |
| | $\beta$ | (34) | (39M) (48T) | | |
| | $\gamma$ | (34) | (48) | | |
| $b$ | $a^*$ | (33A) | (33B) | $a$ | (14) |
| | $b$ | (30) | (31) | | |
| | $c^*$ | (33A) | (33B) | $c$ | (16) |
| | $\alpha$ | (34) | (48) | | |
| | $\beta^*$ | (49) | triangulation | $\beta$ | (21) |
| | $\gamma$ | (34) | (48) | | |
| $c$ | $a^*$ | (33A) | (33B) | $a$ | (14) |
| | $b^*$ | (33A) | (33B) | $b$ | (15) |
| | $c$ | (30) | (31) | | |
| | $\alpha$ | (34) | (48) | | |
| | $\beta$ | (34) | (39M) (48T) | | |
| | $\gamma^*$ | (49) | triangulation | $\gamma$ | (21) |

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# TYPES OF PEGMATITES IN THE ARCHEAN AT GRAND CANYON, ARIZONA

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## ABSTRACT

Granite pegmatites are abundantly developed in the Archean terrane in the Grand Canyon district. They are associated with the youngest Archean granites and appear to be later than the regional deformation. Simple composition is the rule, and complex varieties except for traces of boron facies, are almost unknown. Three types are recognized: the most abundant is similar to the common quartz-microcline pegmatites and is definitely intrusive into a series of meta-sediments and metabasites. A second type has developed by replacement, "pegmatization," processes. A third and very unusual type owes its origin to a late stage development of microcline within a quartz vein or quartz dike. The second and third types are only recognizable as such when the processes to which they owe their origin have stopped somewhat short of complete development. It is possible that many of what are regarded as Type I pegmatites may really be of Type II or Type III.

## INTRODUCTION AND ACKNOWLEDGMENTS

For the past three field seasons the writer, with his colleague Dr. John H. Maxson, has been engaged in an investigation of the Archean rocks in Grand Canyon National Park. The investigation has been made possible by the generosity of the Carnegie Institution of Washington and has been greatly stimulated by the interest and counsel of Dr. John C. Merriam, President of the Carnegie Institution. As regards the particular phase of the investigation discussed herein, it is a pleasure to recall that it was Dr. Charles Palache who first introduced the writer to the fascinating problems of the pegmatites, and it is to Dr. Palache that he owes most of his knowledge of these most interesting structures.

## RÉSUMÉ OF GEOLOGY

The principal contribution to our knowledge of the Archean rocks of this district is due to Noble (1916), who although recognizing and describing many types, both igneous and metamorphic, was uncertain as to the relationships between several of the major units. This was occasioned by the inaccessibility of the critical areas, making detailed examination impossible.

In the present investigation, the work has been very largely confined to the section exposed along the south side of the Colorado river and in its southern tributaries, from Boucher Creek on the west to Lone Tree Canyon on the east, and including an area on the north side of the Colorado in the vicinity of Bright Angel Creek.

Even within this small range, many portions of the section remain inaccessible from the Tonto platform, to which travel must be largely confined. For this reason, conclusions as to the major field and structural relationships of the units described are necessarily tentative. It is hoped that both the range and the completeness of observations may be greatly extended during the coming season. The present paper therefore does not purport to be a complete and final statement as regards any of the rock types. It is given at this time simply to set forth certain interesting relationships that can be demonstrated with the data at hand.

Within the area studied, the Archean history resolves itself into the following sequence:

First: deposition, upon a terrane still virtually unknown, of some thousands of feet of sediments, chiefly argillites and fine-grained sandstones. Near the end of this period of sedimentation, volcanism became active and toward the top of the section basaltic lavas were intercalated. Some of these flows very probably took place as submarine extrusions.

Second: a period of dominant volcanism, in which certainly many hundreds and quite possibly some thousands of feet of basaltic lava accumulated. Sedimentation was greatly interrupted but sandstones, argillites and possibly some cherts were deposited in at least small amount at intervals throughout this period.

Third: intense orogenic disturbance, "Arizonan" of Hinds (1936), whereby the sediments and lavas were strongly folded and very considerably metamorphosed.

Fourth: perhaps concomitant with the declining phases of the orogeny, and very likely continuing after it, came intrusions of granitic magma, which in its upper portions consolidated to form moderately concordant or stock-like masses, and which may have given rise to emanations responsible for "granitization"—the word is used as defined by G. H. Anderson (1937, p. 28)—in the meta-sediments, production of migmatites, etc. The last event of this intrusive period comprises formation of abundant pegmatites and scarcer aplites, many of which develop lit-par-lit structures in the paraschists and metabasites (largely amphibolites).

It is recognized that while some of the granites show marked foliation, others show little or none. This was first noted by Noble (1916, pp. 111–113) who suggested that the first might represent pre-deformation intrusives; the latter, post-deformation intrusives. Within recent years there has been increasing recognition of the fact that many granitic bodies owe their origin to replacement processes, perhaps largely hydrothermal, rather than to direct magmatic invasion. Quirke and Collins (1930) in Ontario, A. L. Anderson (1934) in Southern Idaho, Stark (1935) in the Sawatch Mountains, Kessler (1936) in South Carolina and G. H.

Anderson (1937) in the White Mountains of California-Nevada, have recently given convincing demonstrations of this relationship. In a granite formed in such manner, it is to be expected that foliation may be a matter of inheritance rather than of imposition, and the intrusion will actually be later than the development of the schistosity. While it is outside the scope of the present paper to discuss the detailed relationships of the Archean granites, it may be said that the foliated bodies offer strong evidence of replacement origin in such features as gradational boundaries with the enclosing schists, porphyroblastic structure, abundance of albite and myrmekites, etc. It is believed therefore that only one major period of plutonic activity is represented in this district, with the foliated granites due to replacement, the non-foliated bodies due to direct magmatic invasion, and both developing more or less contemporaneously.

Fifth: Ep-Archean Erosion.

## The Pegmatites

Like the granites with which they are associated, the pegmatites are believed to belong to essentially one period of intrusion, and since some are found definitely cutting all other rock types, they can be assigned with confidence to the last stages of igneous activity within the Archean. On the basis of Landes' (1933) classification, all of the pegmatites would fall within the "acid" group. The great majority would also be classed as "simple." However, certain types found do not readily fit into any existing system of classification. Simply for convenience in discussion, and not with any desire to add to or to emend present classifications, three types are recognized.

*Type I, Intrusive Pegmatites.* The commonest type, designated as "intrusive pegmatite," appears superficially to parallel the schistosity of the enclosing rocks, but on closer inspection the dikes frequently can be seen to be transgressive at a low angle, and occasionally they may cut directly across the schistosity. On the basis of their mineralogy, the great majority would correspond with Landes' "simple, acid" type. They consist almost entirely of quartz and microcline*, the latter in crystals ocasionally up to six inches in length. Muscovite is a minor constituent in many dikes, and abundant in a few. It may form plates and books up to 4 or 5 inches in diameter. Magnetite is a not uncommon constituent, sometimes occurring in well formed octahedra up to an inch in diameter. Garnets are infrequently found.

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* First recognition of microcline as the predominant feldspar of these pegmatites is due to Waesche (1933).

Except for a few pegmatites in which black tourmaline is a scant constituent there is nothing to indicate the development of "complex" types. They are in fact notable for their absence.

Aplites occur, and not infrequently, but they are vastly fewer in number, and bulk much less in the individual bodies, than do the pegmatites. Spurr (1923, 309–331), Olaf Anderson (1930) and others have discussed the relationship between pegmatites and aplites. There is much here that is still a puzzle; but the prevailing idea clearly favors a difference in viscosity, dependent in turn on a difference in the amount of volatiles as the essential difference between aplites and pegmatites.

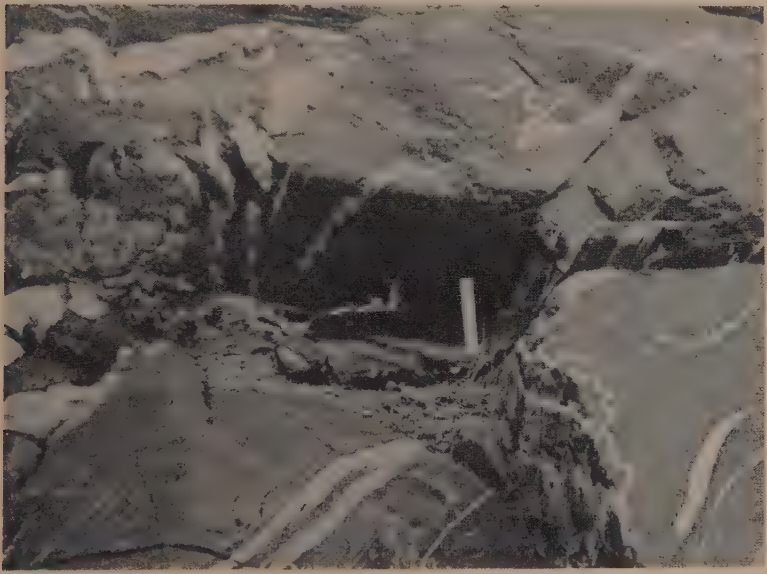

Fig. 1. Type I pegmatites in hornblende-schist, Phantom Creek. The great majority are approximately conformable with the schistosity of the country rock. A few are distinctly cross-cutting, and it is in these that ptygmatic folding is often conspicuously developed.

The fact that pegmatites are relatively abundant, aplites relatively scarce, within this terrane, would argue in favor of a rather "wet" magma. Why, with large supplies of volatiles, there is not more evidence of hydrothermal effects within the pegmatites; why there are no concentrations of the minerals characteristic of the complex pegmatites cannot be answered. A suggestion might be that the portions now exposed represent a section close to the roots of the pegmatites while effects due to more mobile solutions would expectably be found in the higher parts of the structures removed in the Ep-Archean erosion. Donnelly (1936) has recently indicated such a relationship for the more gem-worthy portions of the Pala pegmatites, and the principle is of course frequently applied in the case of the larger plutonic structures (Butler, 1915; Shand, 1922).

An alternative explanation of the barren character of these pegmatites may be found in the suggestion of Eskola (1930) that palingenic magmas are notably "sterile," and it is not improbable that the Archean granites are in large part palingenic.

*Type II, Replacement Pegmatites.* A second type of pegmatite which in theory may seem distinct from the first, but which in actual practice is often impossible to differentiate, is designated "replacement pegmatite." This type has formed in a manner entirely similar to the granitic bodies originating by "granitization" and by analogy these pegmatites might be described as formed by "*pegmatization*" of favorable horizons in the schists. The evidence for such origin is similar to that indicating granitization in the granites. Here, too, one frequently finds gradational boundaries with the country rock. Biotite is much commoner in pegmatites believed to belong to Type II than it is in Type I. Much of this mineral may represent recrystallization of the finer grained biotite of the original mica schist. In the coarse foils in which it occurs, it shows no tendency to alignment. On the other hand, a helizitic structure is sometimes found in which tiny inclusions of muscovite in linear and parallel arrangement indicate the former schistosity of the rock, despite the formation of heterogeneously oriented metacrysts of albite and quartz in which these inclusions occur.

Albite, either alone or with microcline is the chief feldspar of these pegmatites. Some of its appears as perthitic patches in the microcline, but the larger part is in distinct units. It is not the cleavelandite variety so sommon in complex pegmatites, but develops in metacrysts of simple form and stubby or equant shape. In hand specimen it often shows a reddish color similar to that commonly developed by microcline, and indeed it is indistinguishable from the potash feldspars except under the microscope. The red color appears to be due to minute flakes of an iron oxide disseminated, without any obvious crystallographic control, through the mineral. This recalls the hydrothermal albite of certain aplite dikes, recently described by Bastin (1935). He ascribed the formation of hematite to destruction of ferromagnesian minerals in the original diabase which the albite aplites had replaced. In the present instance, the origin of the included hematite is not clear.

Much work remains to be done, and many occurrences must be sampled before any criteria can be established that will serve to distinguish unequivocally between Type I and Type II pegmatites. It is obvious that evidence of pegmatization can never hope to be as satisfactory as evidence of granitization may sometimes be. The coarser the crystallization or recrystallization, the less the chance that any palimpsest structures will survive to indicate the origin of the rock. Field boundaries in themselves mean little, for many definitely intrusive pegmatites show gradational walls; while it is to be expected that many replacement pegmatites will show sharp boundaries against enclosing schist. The mere occurrence of albite signifies little, for although many will agree with Bowen (1928) in considering this mineral to be almost invariably of secondary development, its presence in a pegmatite indicates only the operation of a replacement process to limited degree, and does not prove that the entire structure is due to pegmatization. Indeed, unless definitive relict structures can be found there is little opportunity for certain recognition of a Type II pegmatite.

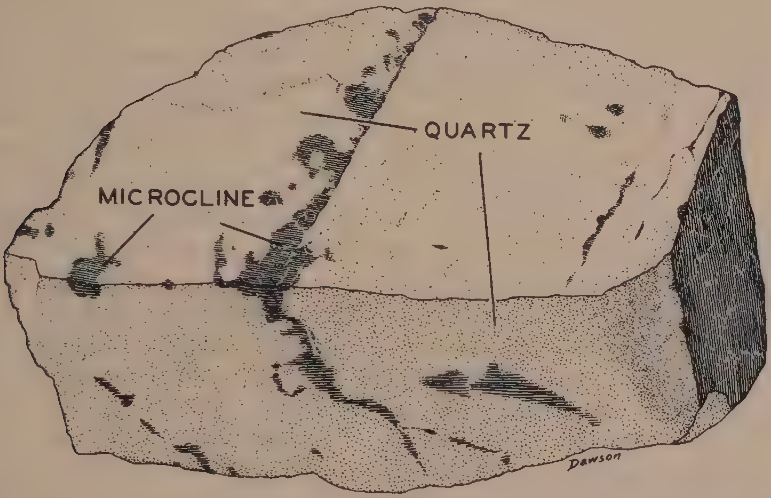

FIG. 2. Sketch of hand-specimen of silexite from Clear Creek. This shows the incipient stage in the development of a Type III pegmatite.

*Type III, Feldspathized Quartz Veins.* Occasionally pegmatites seem to give way to rocks best described as silexites. They are composed almost entirely of quartz, but an occasional crystal of pink feldspar occurs. Such facies occur notably in Lone Tree Canyon and near the mouth of Boucher Creek where as shown by Campbell and Maxson (1935) the section consists largely of paraschists showing less intense metamorphism than elsewhere in the district. There is nothing unusual in finding quartz dikes apparently gradational with pegmatites. Spurr (1923) has described numerous instances, and the literature has been more recently summarized by Tolman (1931). In practically all such cases, the assumption is that the pegmatite grades, by diminution of feldspar, into silexite and eventually into a quartz "dike" or vein. The discovery of the silexite dikes in Lone Tree Canyon and in Boucher Creek seems entirely compatible with a location farther from the "hot centers" of metamorphism as is indicated by the character of the surrounding rocks and the absence of granite intrusives.

In some instances tiny pink veinlets may be seen threading through the silexite. These were dismissed at first with little attention and attributed to a supergene oxidation along fractures. Further observations however compelled recognition of the veinlets as feldspathic material, definitely later than and replacing quartz, which when developed to sufficient extent, yielded a rock to all appearances the equivalent of any of the simple pegmatites. It was confidently expected that this vein feldspar would turn out to be albite; but microscopic examination clearly indicates microcline. The indices of refraction correspond exactly and while portions are untwinned, the characteristic quadrille twinning is frequently developed.

The quartz of the silexites appears similar to that of the pegmatites, crystallizing in coarse anhedrons with an abundance of minute bubble-like inclusions. Strain shadows and small fractures are common; but there is no granulation. Adams (1921) has discussed the characters of vein quartz, and this shows no marked resemblance to any of the more distinctive vein textures. On the other hand, Tolman (1931) from his study of quartz bodies of igneous origin concluded that there were few positive criteria by which such quartz could be explicitly distinguished. Whatever may be the origin of the quartz in the silexites, the interesting and almost unique feature is the time relationship between the quartz and the microcline. In the better defined examples and in the incipient stages of the process (see fig. 2) there can be no question of the secondary (doubtless hydrothermal) nature of the microcline. The same relationship is observable also in thin section. Microcline, along with quartz has of course long been recognized as one of the last minerals to crystallize in the normal sequence in igneous rocks. Where found in pegmatites, however, it is very generally considered one of the first, if not indeed the very first mineral to crystallize. Schaller (1927) has indicated that in such rocks a high temperature potassium feldspar (probably orthoclase) was the first constituent to form; that this reverted on cooling to microcline; and that the quartz (even the quartz of the graphic intergrowths) is secondary to this.

In the present cases, this relation is reversed; for microcline belongs to a distinctly later generation than the quartz, which it clearly replaces. Instances of feldspathization of quartz are by no means unknown. Anyone who has studied veins characteristic of the epithermal zone can recall many instances of adularia developing at the expense of quartz and other constituents of the rock or vein in which it occurred. This to be sure is rather different from the case under consideration. An interesting example of feldspathization, although again not strictly analogous, is described by Reynolds (1936) from Colonsay. She has also summarized occurrences in which there has been feldspathization of quartz or quartzite. In the Colonsay example quartzite xenoliths have been feldspathized, largely with the development of perthites (the albite is secondary to the potash feldspar of the perthite) and what corresponds to syntectic pegmatite is developed on a small scale.

In the present case, the source of the feldspar, whether magmatic, syntectic, palingenic, etc., is as much or more uncertain than the source of the quartz. Nor is there, in view of the marked time difference between these two minerals, any assurance that they are in any way related to a common source. Microcline is regarded by many as a strictly pyrogenic mineral; but its structural relationships in these occurrences would place it as more likely to be hydrothermal.

In view of their apparent distance from any of the larger granite masses of the area, it was an obvious suggestion that these pegmatitic silexites might have originated by palingenesis. Daly (1914) has said: "During intense regional metamorphism . . . deep-seated rocks charged with much interstitial water may reach the relatively low temperature at which minerals corresponding to the quartz-feldspar eutectic go into solution with the water and other volatile fluxes. Such small, locally generated pockets, lenses or tongues of fluid may be driven through the solid country rock for an indefinite distance; subsequently to crystallize with the composition and habit of true batholithic derivatives." That the Type III pegmatites here described might have originated in some such manner is disproved by the proportions of the quartz and feldspar which are in no way comparable to those of the eutectic suggested by Vogt (1931, p. 423). On the other hand, that these are "batholithic derivatives" is by no means clear: the time relationships of the quartz and the microcline are not readily compatible with such an origin. That they are bedding plane quartz veins developed early in the history of the meta-sediments in which they are found, and have since been feldspathized, is not impossible. But it should be mentioned that these veins at times show the curious crenulations and irregularity of structure (found also in the Type I and Type II pegmatites) to which Sederholm (1913) has given the name of "ptygmatic folds." Such a structure is interpreted by some geologists (Grout, 1932, p. 360) as requiring injection during deformation. Bedding plane quartz veins would not, on this hypothesis, develop ptygmatic folds.

What the quantitative importance of the Type III pegmatites may be is uncertain. As was the case with the Type II structures, a complete development entirely obscures the origin, and it is quite possible that many Type I and Type II pegmatites may actually have developed in the manner indicated for Type III, viz., replacement by microcline of what was originally a quartz vein.

## Summary and Conclusions

An increasing opinion and body of knowledge indicates that granite may have formed in several ways other than by direct invasion of primary magma. Eskola (1932) and Collins (1933) have contributed noteworthy discussions on this subject. With the close association known to exist between granite and pegmatite, it is only reasonable to expect that pegmatites may also have formed initially in ways other than by simple intrusion.

Emphasis in recent years has been placed on the long and complex cooling history frequently shown by pegmatites. It now seems probable that the initial formation of pegmatites may in some cases be as complex as is their later history. This has been anticipated to a certain extent by Schaller (1933) who said: "Notwithstanding the fact that all writers on pegmatites seem to accept their origin as being directly related to end products of differentiation of magmas, it will not be amiss to call attention to the possibility that they may represent the 'sweat,' or the most easily liquefied portions that have been squeezed out of various kinds of rocks by orogenic processes."

Because of their coarser crystallization and occasionally more complex history, pegmatites will not in general indicate their true origin as clearly as is sometimes the case with granites. Nevertheless in the Archean area in Grand Canyon evidence exists suggesting three possible modes of origin: by magmatic intrusion; by "pegmatization"; and by hydrothermal feldspathization of quartz veins. Only under very fortunate circumstances, or else in the incipient stages of development can the second and third types be unequivocally distinguished from the first.

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# A NEW LAW OF CRYSTAL MORPHOLOGY EXTENDING THE LAW OF BRAVAIS

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## Contents

The Law of Bravais . . . . . 446
Space Group Symmetry . . . . . 447
The Effect of a Screw Axis . . . . . 449
    Example: Low Quartz . . . . . 450
The Effect of a Glide Plane . . . . . 451
    Example: Orthorhombic Sulfur . . . . . 452
Statement and Discussion of the Generalized Law . . . . . 454
Discrimination between Complementary Merohedral Forms . . . . . 456
    Example: Pyrite . . . . . 457
Space Group Determination by Morphological Criteria . . . . . 460
    Examples: Garnet . . . . . 460
        Analcime . . . . . 461
        Spinel . . . . . 462
Persisting anomalies . . . . . 463
    Example: Halite . . . . . 463
Summary . . . . . 465
References . . . . . 466

## The Law of Bravais

This law, proposed by Bravais on speculative grounds, only received general acceptance after Georges Friedel (1904, 1905, 1907) proved it to be substantiated by observation. With certain restrictions the law states that, for any crystalline species, a translation lattice can be found such that: (1) The observed crystal faces are parallel to the net planes with the highest reticular densities (or smallest mesh areas); (2) the greater the reticular density (or the smaller the mesh area) the more important the corresponding form.

The importance of a form is estimated from its size, frequency of occurrence, and presence as a cleavage form. The *reticular density* of a net plane *hkl* is defined as the number of lattice points (nodes) per unit surface. It is inversely proportional to the *reticular area*, or area $S$ of the smallest mesh in the net, and directly proportional to the *interplanar distance* $d$, since $S \cdot d = V$, where $V$, the volume of the smallest unit cell, is a constant for any lattice.

Morphologists of the French School have advocated the acceptance of the lattice indicated by the Law of Bravais, in preference to any other lattice that would also give the observed forms reasonably simple Miller indices. The lattice chosen on this basis has been called the "Haüy-Bravais lattice" or "morphological lattice," in contradistinction to the "structural lattice" or true translation lattice, determined by $x$-ray technique. This nomenclature stresses the baffling fact that the two lattices are not always geometrically similar.

Known objections and restrictions to the Law of Bravais include the following:

(1) The forms present on a crystal do not depend only on factors within the crystal, but on external factors as well (conditions of crystallization). A statistical survey of morphological data (locality persistence, in Niggli's sense) usually suffices to detect the influence of external causes, which can then be left out of consideration.

(2) Even in the most favorable instances the law holds for dominant forms only. Minor forms are always irregularly scattered down the list of decreasing theoretical importance.

(3) Frequently the best lattice that can be arrived at leads to an order of importance not wholly satisfactory for the dominant forms and it may even assign small mesh areas to unknown or insignificant forms.

(4) Cleavage forms do not always coincide with the largest and most frequent crystal forms, and conversely.

(5) Complementary merohedral forms have the same mesh area, yet do not always show equal morphological importance.

These objections have given the Law of Bravais the status of a first approximation. G. Friedel, who conceded this point, foresaw an explanation for the encountered anomalies in the "perturbing influence" of the *motif* (the contents of the unit cell).

In this paper we propose to state a law[1] that takes into account one of the important properties of the motif—its symmetry.

## SPACE GROUP SYMMETRY

The 230 space groups were derived by combining, in all possible ways, the different symmetry operations: translation, rotation, and reflection (or inversion). This process involved, among others, two composite symmetry elements, which had not been previously recognized (although they are actually implied in some of the 14 Bravais lattices), namely: the screw axis (Sohncke) and the glide plane (Fedorov, Schoenflies, Barlow).

In this paper we shall not concern ourselves with those screw axes and glide planes that are inherent in the translation lattice,[2] since their effect is already taken into account by the Law of Bravais. We shall deal only with screw axes and glide planes that can be combined with a translation lattice, in addition to those it may already possess. The distinction between the two kinds of screw axes or glide planes is made in the Hermann-Mauguin notation: those that exist in the lattice itself are implicitly expressed by the Roman capital indicative of the translation group, the others are explicitly symbolized. The effect of the former is to bring a node into coincidence with another node (which could also be reached by applying a translation to, and which is in parallel orientation with, the first). The effect of the latter is to produce additional points within the lattice, points, however, which are not lattice points ( nodes) since they cannot be obtained from any node by translation alone, but only by a translation accompanied by either a rotation or a reflection. Additional points produced by a screw axis are congruent to the true lattice points (nodes), although not in parallel orientation with them; additional points produced by a glide plane are enantiomorphous to lattice nodes. For convenience, in case there are additional points resulting from the action of screw axes and glide planes, we shall term "lattice equipoints" the nodes of the Bravais lattice and "space group equipoints" the additional points.

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[1] A preliminary communication was presented at the January meeting of the *Académie des Sciences* in Paris (1937).

[2] Glide planes and screw axes occur in all the centered modes of all latices, and also in the hexahedral (primitive) mode of the cubic, tetragonal, and hexagonal lattices (we consider the rhombohedral lattice a mode of the hexagonal). The only lattices devoid of

At this juncture one should recall that a node of a Bravais lattice stands for a whole motif (the contents of a complete unit cell, regardless of how matter may be distributed in it) and that the symmetry of the motif cannot exceed that of the parallelopiped outlined by the cell (holohedry), but may be inferior to it (merohedry). When screw axes and glide planes are present the motif (still represented by the "node") may be thought of as split into several fractions or "submotifs" derived from each other by the available screw rotations and glide reflections; any of these submotifs may be represented by the "lattice equipoint," the others are represented by "space group equipoints."

The Law of Bravais defines reticular density in terms of nodes only. It is our purpose to show that, when a node is replaced by a "lattice equipoint" and one or more "space group equipoints,"the reticular density must be defined in terms of "equipoints" for certain faces: the faces perpendicular to a screw axis and some of the faces perpendicular to a glide plane. Inasmuch as the faces affected in this way are determined by the kind and amount of space group symmetry, they become, con-

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inherent screw axes and glide planes are the triclinic (P), the hexahedral monoclinic (P), and the rectangular hexahedral orthorhombic (P). The figures in the *International Tables for the Determination of Crystal Structures* (Chapter V, Space groups) illustrate the presence of screw axes and glide planes in the lattices mentioned.

versely, criteria indicative of such symmetry. Hence, if the symmetry of the space group is known, its influence on the form development can be predicted and checked; *vice versa* it is possible to ascertain with which space group (or set of space groups) observed morphological features are compatible.

## The Effect of a Screw Axis

A screw axis, represented by the symbol $p_q$ in the Hermann-Mauguin notation, is a $p$-fold axis of symmetry, the operation of which is the product of a rotation through $2\pi/p$ and a displacement by a fraction $q/p$ of the shortest translation parallel to the axis. The displacement is known as the *screw component*. The crystallographically possible screw axes are: $2_1$; ($3_1$, $3_2$); ($4_1$, $4_3$); $4_2$; ($6_1$, $6_5$); ($6_2$, $6_4$); $6_3$. Enantiomorphous screw axes, here collected between parenthesis, may be considered as having the same screw component but opposite screw senses. The fraction $q/p$, therefore, will always be of the form $1/n$, with $n=2$, 3, 4, or 6.

Consider any two successive lattice planes perpendicular to a screw axis. Let $d$ be their spacing. These two lattice planes will be interleaved by $(n-1)$ other planes brought about by the action of the screw axis, thus resulting in a system of parallel, equidistant planes with the spacing $d/n$. The lattice planes contain "lattice equipoints" only, the intervening planes "space group equipoints" only. The arrangement of equipoints in any two successive planes of the complete system is the same except for the $2\pi/p$ rotation. All the planes of the system will, therefore, be geometrically equivalent insofar as concerns the crystal form (pinacoid) that parallels them. For such a pinacoid, the faces of which are perpendicular to a screw axis, the "effective" spacing is $d/n$ instead of $d$. Formally, by virtue of the relations between spacing, reticular density, and mesh area, it is equivalent to consider that the reticular density should be divided by $n$ or the mesh area multiplied by $n$. Either one of these artifices will adequately express true morphological importance. No other crystal forms, besides the pinacoid just discussed, can parallel equidistant planes containing equipoints of the same sort only; their morphological importance, therefore, cannot be altered. These conclusions are verified by observation.

The reticular area $S$ is given by the formula

$$\begin{aligned}S_{\mathrm{hkl}}^2 &= h^2S_{100}^2+k^2S_{010}^2+l^2S_{001}^2\\ &+2(hkS_{100}S_{010}\cos\nu+klS_{010}S_{001}\cos\lambda+lhS_{001}S_{100}\cos\mu),\end{aligned}$$

in which $S_{100}=bc\sin\alpha$, $S_{010}=ca\sin\beta$, $S_{001}=ab\sin\gamma$; and $\lambda=(010):(001)$, $\mu=(001):(100)$, $\nu=(100):(010)$. Hence, the value of $S$ will be multiplied by any number $n$ if all three indices are multiplied by $n$. We propose generally to adopt this convention and to designate by the symbol $(nh \cdot nk \cdot nl)$ any face $(hkl)$ normal to a screw axis, with screw component $d/n$. The classical symbol $(hkl)$ merely indicates the face direction. The suggested symbol $(nh \cdot nk \cdot nl)$ acquires a further value—that of a quantitative estimate of the form importance, since the mesh area $S$ is directly obtainable from the "multiple indices" (by introducing them as such in the formula giving $S$ or so-called "quadratic form" $S^2$). The Miller notation, thus but little modified, assumes greatly enhanced morphological significance.[3]

*Example of the Screw Axis Effect: Low Quartz.* Hexagonal trapezohedral class ($D_3 = 3\ 2$). Axial ratio: $c/a = 1.1000$. As demanded by the Law of Bravais and confirmed by $x$-ray determination,[4] the translation lattice is hexagonal (*not* rhombohedral) and the point group symmetry must be considered holoaxial tetartohedral (*not* holoaxial hemihedral). $a_0 = 4.89$ A.U., $c_0 = 5.38$ A.U. The space group is one of the enantiomorphous pair $D_3^4 = C3_12$ and $D_3^6 = C3_22$.

The 3-fold symmetry axis is a screw axis, whose screw component is $c_0/3$. The basal pinacoid must be written $\{0003\}$ instead of $\{0001\}$. Its mesh area is trebled, or its reticular density divided by 3. In the Bravais sequence of theoretical importance, the base came first ($S_{0001} = 1.13$). In the modified list, it goes down to the eighth place ($S_{0003} = 3.39$), after $10\bar{1}0$, $10\bar{1}1$, $11\bar{2}0$, $10\bar{1}2$, $11\bar{2}1$, $20\bar{2}1$, $11\bar{2}2$ (no distinction is made here between merohedral forms).

Thus is explained the extreme rarity of the basal pinacoid in quartz, one of the most striking morphological characters of the species and a flagrant anomaly to the Law of Bravais.

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[3] H. Ungemach (1935), in order to stress the unity of the hexagonal system *sensu vasto*, in the light of recently discovered examples of syntaxy, proposed to use the 4-index Bravais symbols $(hk\bar{i}l)$, slightly modified by the omission of the minus sign over the third index, for crystals having a rhombohedral lattice, with the provision that all four indices should be multiplied by 3 when the sum $h+i+l$ is not a multiple of 3. Examples: (0003), (3030). This amounts to considering the rhombohedral lattice a mode of the hexagonal lattice. M. A. Peacock and M. C. Bandy (1936) followed the suggestion in calling the cleavage of their new mineral ungemachite {0003} {111}.

J. D. H. Donnay (1936) proposed to extend the practice to all systems where the lattice may have more than one mode. Examples.—In the body-centered mode of the cubic lattice, multiply all three indices by 2 if their sum is not even: (110), (200), (211), (222), etc. In the face-centered mode, double all three indices if they are not all odd: (111), (200), (220), (311), etc. Such a procedure expresses the Law of Bravais only.

In the present paper we generalize the symbolization so as to include the effect of screw axes and glide planes.

[4] All the structural data quoted in this paper are taken from *Strukturbericht*, where more specific references may be found.

## THE EFFECT OF A GLIDE PLANE

A glide plane is a plane of symmetry, whose operation is the product of a reflection in the plane and a displacement parallel to the plane. The displacement is known as the *glide component*. The possible glide components are (in vectorial notation): $\frac{1}{2}$ **a**; $\frac{1}{2}$ **b**; $\frac{1}{2}$ **c**; $\frac{1}{2}$ (**a**+**b**), $\frac{1}{2}$ (**b**+**c**), $\frac{1}{2}$ (**c**+**a**); $\frac{1}{4}$ (**a**±**b**), $\frac{1}{4}$ (**b**±**c**), $\frac{1}{4}$ (**c**±**a**). The Hermann-Mauguin notation of a glide plane is obtained by replacing, in the point group symbol, the letter *m* indicative of a reflection plane of symmetry by one of the letters *a*, *b*, *c*, *n*, *d*, chosen according to the type of glide component.

Consider a glide plane in an othorhombic primitive lattice (hexahedral mode), parallel to any one of the coordinate planes, for instance (100). Let the glide component be parallel to either one of the two coordinate axes in the plane, for example $\frac{1}{2}$ **b**. The effect of the glide plane will be to bring space group equipoints into the centers of the (001) meshes. (See Fig. 1, where the glide plane is parallel to the plane of the figure, the lattice equipoints are represented by white circlets, the space group equipoints by black dots.) The space group equipoints are in enantiomorphous relation to the lattice equipoints. No new points are introduced between successive (001) planes—the spacing of the latter remains unchanged. In the (001) planes the motif comprises both the lattice equipoint and the space group equipoint derived from it by glide reflection—the translation net of (001) remains what it was, its mesh area has not changed, neither has its reticular density. The same observation applies to all planes that contain both space group equipoints and lattice equipoints, *e.g.*, the system of planes (021).

Among the systems of net planes (0*kl*) perpendicular to the glide plane, there are some that contain one kind of points only, either lattice equipoints or space group equipoints, *e.g.*, the system of planes (011). In any such system of planes, true lattice planes (beset with lattice equipoints only) alternate with other planes (occupied by space group equipoints only). Any two successive planes can be considered geometrically equivalent since they contain identical nets with motifs similar in all respects except for the fact that they are mirror images of each other (the motif of true lattice planes being represented by a lattice equipoint, that of intervening planes being figured by its enantiomorphous "space group equipoint"). For any crystal face that parallels such a system of planes, the "effective" interplanar spacing should be taken as one half of the distance between true lattice planes if it is to express morphological importance; one may as well say that the reticular density should be halved or the mesh area *S* doubled. According to the proposed symbolization the indices should be multiplied by 2, so that (011) is to be written (022). More generally, all the planes ($0kl$) that contain points of the two different kinds are those that fulfill the condition $k=2n$. Those that do not satisfy this condition must have their indices multiplied through by 2. Since $h=0$ for all planes perpendicular to the glide plane, the condition may be written $h+k=2n$, which is the criterion of a lattice centered on (001). We may thus express this result by saying that the lattice acts as a $C$-centered lattice for all faces in the zone [100].

If, in the above example, the glide component had been taken equal to $\frac{1}{2}$ **c**, the lattice would have acted as a $B$-centered lattice for all faces in zone [100].

When the glide plane is parallel to (010) and the glide component is $\frac{1}{2}$ **c** or $\frac{1}{2}$ **a**, the lattice acts as if $A$-centered or $C$-centered, respectively, for all faces in zone [010]. Again, if the glide plane is (001), the effective lattice for the faces of zone [001] will be either $B$-centered or $A$-centered according as the glide component is $\frac{1}{2}$ **a** or $\frac{1}{2}$ **b**.

A glide plane $n$, whose glide component is one half the resultant of the two primitive translations in that plane, *e.g.*, $\frac{1}{2}$ (**a**+**b**), transforms a $P$ lattice (primitive) into an $I$ lattice (body centered) insofar as faces perpendicular to $n$ are concerned.

Similar propositions could be established for all space groups where glide planes occur, invariably leading to the recognition of certain planes (among those perpendicular to the glide plane) whose morphological importance is to be decreased. Such a diminished importance is expressed by a multiplication of the indices so as to comply with the restrictions imposed by the presence of the glide planes. These conditions may be combined with others, resulting from the occurrence of screw axes, or due to the different types of centering of the lattice. It is easily seen that such combined conditions are precisely those that the various orders of $x$-ray reflections must fulfill in order to escape destructive interference (systematic "extinction," *Auslöschung*). These conditions, worked out by structural crystallographers, are directly available in any table of "space group extinctions."

Our conclusions as to the effect of a glide plane are verified by observation.

*Example of the Glide Plane Effect: Orthorhombic sulfur*. Rhombic dipyramidal or orthorhombic holohedral class ($D_{2h}=2/m\ 2/m\ 2/m$). Axial ratios—$a:b:c=0.8131:1:1.9034$. As demanded by the Law of Bravais and confirmed by $x$-ray determination, the translation lattice is all-face centered (rhombic octahedral mode). $a_0=10.61$ A.U., $b_0=12.87$ A.U., $c_0=24.56$ A. U. The space group is $D_{2h}{}^{24}=Fddd$.

The space group criteria include the conditions expressing the all-face centered mode of the lattice, namely: $h+k=2n$, $k+l=2n$, $l+h=2n$, or in other words "$h$, $k$, $l$ either all odd or all even." For planes whose indices include at least one zero this condition becomes "indices all even." In addition to this first criterion the presence of the glide planes $d$ demands, for those planes whose indices contain at least one zero, that the sum of the indices be a multiple of 4, namely: planes $(0kl)$ with $k+l=4n$, planes $(h0l)$ with $l+h=4n$, planes $(hk0)$ with $h+k=4n$. In accordance with our symbolization by means of "multiple indices" the list of crystal forms according to the Law of Bravais will only contain symbols with indices all odd or all even (indices not all odd are made all even by multiplying through by 2). The first two columns of Table 1 (headed "B–F" and "Com") give the Bravais list in such a form. In order to take the glide plane effect into account, form symbols whose indices include at least one zero, and which are already doubled by virtue of the all-face centered lattice (Law of Bravais), should be multiplied by 2 again if necessary to make the sum of their indices a multiple of 4. The mesh area of

TABLE 1. ORTHORHOMBIC SULFUR

Space group: $D_{2h}^{24}=Fddd$

| B-F | Com | D-H | B-F | Com | D-H | B-F | Com | D-H |
|---|---|---|---|---|---|---|---|---|
| 002 | — | | | 135 | | | *424 | |
| | 111 | | | 315 | | | *139 | |
| 020 | — | | *028 | — | | | 155 | |
| | — | 004 | 260 | — | | | — | *048 |
| | 113 | | | 331 | | | *2.0.10 | |
| | 022 | | | *242 | | *406 | — | |
| 200 | — | | *208 | — | | | ?1.1.11 | |
| | 202 | | | *137 | | | 337 | |
| *024 | — | | | — | 400 | | 319 | |
| | 115 | | | 119 | | | ?062 | |
| | 220 | | *402 | — | | | *426 | |
| 204 | — | | 046 | — | | | *351 | |
| | 131 | | | 244 | | | *511 | |
| | 133 | | | 151 | | | *248 | |
| | 026 | | | 223 | | | *157 | |
| | 224 | | | *317 | | *064 | — | |
| | 311 | | *420 | — | | | *353 | |
| | 206 | | | *153 | | | *513 | |
| | — | 040 | | 422 | | | 442 | |
| | 117 | | | 335 | | | 260 | |
| | 313 | | | *0.2.10 | | | — | 408 |
| *042 | — | | | *246 | | *0.4.10 | — | |

N.B. Crystal forms that have not been observed on sulfur are preceded by an asterisk (*). Doubtful forms are shown by a question mark (?).

such forms is thus quadrupled by the new law instead of simply doubled as it was by the Law of Bravais. The new sequence is shown by the last two columns (headed "Com" and "D–H") of Table 1. The second column in this table contains the forms common to both sequences of decreasing theoretical importance (Bravais-Friedel, on the one hand; Donnay-Harker, on the other).

The example of sulfur was given by G. Friedel (1926, p. 133) to illustrate the finding of the translation lattice by means of the Law of Bravais. Friedel stresses the presence of certain anomalies in the list, namely the fact that the forms {012} and {102} are unknown[5] for the species, in spite of their relatively small mesh areas. The next two gaps, those of {021} and {014}, occurring among observed forms, are just as anomalous. Moreover the order of the forms does not fit the facts satisfactorily: {001} occupying the first rank implies a tabular habit, which has been observed occasionally, but is by no means representative of the majority of sulfur crystals; the other two pinacoids are also placed too high in the sequence with respect to their minor morphological importance.

The modified law (see Table 1), doubling again the mesh area of the forms in the first column, causes them to recede in the list to ranks more in keeping with their observed importance. The pinacoids become {004}, {040}, and {400}. The first four missing forms become {048}, {408}, {084}, and {0.4.16}, and are relegated far down the list. The rhombic dipyramid {111} takes first place, as one would expect of the habit-controlling form. The first unknown form is the 20th in the new list, against the 8th in the Bravais sequence.

## STATEMENT AND DISCUSSION OF THE GENERALIZED LAW

The relationship that exists between the systematic "extinctions" of certain orders of $x$-ray reflection in a given space group and the diminished importance of corresponding crystal forms permits the following statement of the law:

*The morphological importance of a crystal face is inversely proportional to its reticular area S if the lattice is of the hexahedral mode (no centering) and the space group symmetry does not contain any screw axis or glide plane. The effect of lattice centering, screw axes, and glide planes is corrected for if the face indices are replaced, in the S formula, by the "multiple indices" of the lowest order of x-ray reflection compatible with the space group symmetry.*

Instead of considering the mesh area of a plane, it is largely a matter of personal preference to consider its reticular density or its spacing to the next parallel plane in the system, either one of the last two quantities being inversely proportional to the mesh area.

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[5] The form {102}, it is true, has been reported since, but it remains a morphological rarity.

The law includes the Law of Bravais as a particular case, when, regardless of lattice centering, the space group symmetry is devoid of screw axes or glide planes. It is an extension of the Law of Bravais in the sense that it rests on the same kind of geometrical considerations. The difference is that the reticular constant of a face (its mesh area, reticular density, or interplanar distance) is no longer calculated in *the* translation lattice, but in a variable system of points, changing with the face or zone considered. For instance, in the tetragonal space group $D_{4h}^3 = P\ 4/n\ b\ m$, where the translation lattice actually is primitive tetragonal, the reticular constant is computed as if the lattice were body centered ($I$) for faces ($hk0$), base centered ($C$) for faces ($0kl$), simple ($P$) for faces ($hhl$), while for faces ($hkl$)—and this is a general rule—the reticular constant is still to be determined in the true translation lattice.

The new law thus brings out the fundamental importance of zonal development in crystal morphology, a fact which had been anticipated by previous crystallographers (Baumhauer, 1903–1905; Ungemach, 1934 and 1935). It confirms the interest of the investigation of "form series" (Baumhauer's *Zielreihen*, Ungemach's *séries zonaires*, Peacock's *Harmonic-Arithmetic Rule*, 1936).

The law cast in the above statement may, up to a certain point, be said to bridge the gap that existed between structural and morphological crystallographies. It is a further step in the elucidation of the control that the internal pattern of a crystal exercises on its bounding forms. Yet it does not involve any consideration of the special positions that the atoms may occupy, nor does it take into account their nature, their charge, their bonds, or any other physical concept. It only makes use of the "empty frame" of symmetry elements in the cell—it is, in essence, purely geometrical.

Since so many factors are ignored that may well be expected to play a role in the development of crystal forms, the law can claim no other value than that of an improved approximation. Not all the anomalies will be eliminated, as it is easy to foresee that several consequences of the law will not be verified. (1) If space group symmetry were the only influential factor, then all crystalline species belonging to the same space group of the isometric system (where the axial ratios and angles are constant) would have an identical list of forms arranged in the order of decreasing importance, or the same "morphological aspect," as we propose to call such a sequence. (2) Several space groups obey the same general conditions of systematic extinction, thus leading to the same "morphological aspect" for, say, merohedral as well as holohedral species. (3) The generalized law does not discriminate between complementary merohedral forms in all cases. (4) Anomalies may also result from the fact that no provision is made for differences in the conditions of crystallization (rate of cooling, presence of foreign ions in the solution, and the like) in spite of the attempt to eliminate such external factors by a critical examination of available morphological data.

In his masterly work on the subject, Friedel (1907) proved that the influence of the Bravais lattice is so preponderant that it rarely becomes obscured by that of the motif. Now a painstaking survey of a great many crystalline substances for which the space group is known conclusively shows that, although the symmetry of the space group cannot be the only factor either, it so outweighs all the others in influence that its effect, in the large majority of cases, is not obliterated by the action of the disturbing agents. This result, incidentally, will rehabilitate the symmetry (or pseudo-symmetry) of crystals as one of their most significant properties, a notion which of late had lost more and more credence among structural crystallographers.

Apart from any merit that may be conceded or refused to our speculations on the effect of screw axes and glide planes, the outcome of our statistical survey warrants considering the generalized form of the Bravais principle as a law of observation, valid independently of any theory.

This law leads to the recognition of a great many more "morphological aspects" than did the Law of Bravais. We define a "morphological aspect" as a possible list of decreasingly important forms for any set of axial elements (axial ratios and interaxial angles) in any given crystal system. For instance, in the isometric system, the Law of Bravais led to 3 morphological aspects; the present law leads to 17. These are invariable since cubic axial elements are constant. A "morphological aspect" corresponds to a certain set of general extinction conditions, which characterize one space group or may be common to several space groups. There are, therefore, as many "morphological aspects" possible as there are different sets of systematic space group extinctions. They will be presented, for each crystal system, in later publications.

The next sections will illustrate by examples (chosen among isometric substances) the separation of complementary hemihedral forms and the determination of the space group from morphological data. An anomalous case, that of sodium chloride, will also be discussed.

## Discrimination between Complementary Merohedral Forms

Since the Law of Bravais is based on the consideration of the lattice only, it cannot make any distinction between complementary merohedral forms. The introduction of space group symmetry enables one to separate (in some cases, at least) complementary hemihedral forms.

*Example: Pyrite*, $FeS_2$. Isometric system. Diploidal or parahemihedral class ($T_h = 2/m\,\bar{3}$). $a_0 = 5.40$ A.U. The translation lattice is hexahedral (no centering). The space group is $T_h^6 = Pa3$.

None of the three Bravais lists available in the isometric system, corresponding to the three possible lattice modes, is very satisfactory. The agreement with observed form importance is the least bad in the hexahedral mode (simple cubic lattice), which places {012} at the fourth rank. In spite of many anomalies, the correct translation lattice was thus arrived at by the Law of Bravais.

According to the space group criterion the forms $\{0kl\}$ must satisfy the condition $k = 2n$. If they do not their indices are doubled. This condition separates some complementary pyritohedra; for instance, {021} should have more importance than {012}, which is to be written {024}. The Bravais sequence and the modified list are compared in Table 2. Thefirst column (headed "Bravais-Friedel") gives the Bravais list, which does not discriminate between complementary forms. The second column (headed "Donnay-Harker") gives the new order, in which most of the complementary pyritohedra are separated. The third column (headed "Comparison") presents the data in the same manner as Table 1 for sulfur. In the modified sequence the first three forms are the three most important forms, the first two are the only cleavages (imperfect though they may be). The dominant forms in artificial pyrite crystals are the cube and the octahedron (Groth, 1921, p. 257: "Die nach verschiedenen Methoden erhaltenen Krystalle zeigen meist (100) and (111)").

Two complementary pyritohedra will have equal importance when their symbols contain two odd indices besides the zero; they will be separated if only one of the indices is odd. The data recorded in the standard compendia of mineralogy are insufficient to check the validity of this prediction of the law. Discrimination between positive and negative forms is often uncertain. Hintze (1904) does not attempt to make the distinction. V. Goldschmidt (1920) makes it for a few forms only. Strüver's suggestion that the distinction between positive and negative forms be drawn only if two forms of different sign occur together, in which case the larger and more brilliant one is to be taken as positive, is an arbitrary criterion, at best unsatisfactory. The verification of the law is fortunately made possible by H. Ungemach's valuable observations on form importance in pyrite crystals.[6] It is remarkable that information can thus be obtained on the first *eleven* pairs of pyritohedra that are to be separated by the space group criterion. Here are Ungemach's data: {021} overwhelmingly more important than {012=024}; {023} vastly more than {032=064}; {041} much more than {014=028}; {043} probably more than {034=068}; {025} less important than {052=0.10.4} (anomaly); {061} known, {016=0.2.12} unknown; {045} much more important than {054=0.10.8}; {027} unknown, {072=0.14.4} known (anomaly); {065} much more important than {056=0.10.12}; the next four pyritohedra, {081}, {018=0.2.16}, {047}, {074=0.14.8} are known, but are minor forms whose relative importance cannot be estimated from Ungemach's projection (they are all represented by small points). The first three pairs of complementary pyritohedra show perfect agreement between facts and theory. Notice that {023} is a negative form, predominant over its positive complementary.

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[6] Unpublished data of the great French crystallographer and mineralogist (1880–1936), found in the note books he bequeathed to J. D. H. Donnay. The observations are graphically recorded on a work sheet, a gnomonic projection of pyrite showing the

A strange fact is revealed by an inspection of the pyritohedra with two indices odd, which should have equal morphological importance: the two complementary forms coexist in three cases only, {075}, {0.15.11}, {097}; the negative form is found alone once, {0.7.11}; the positive form occurs alone in fourteen cases, {091}, {071}, {0.17.3}, {051}, {0.11.3}, {031}, {073}, {0.11.5}, {0.15.7{, {0.13.7}, {095}, {053}, {0.13.9}, {0.11.9}. These data conflict with the theory. It should be noticed, however, that the pair {013=026} {031=062} that is encountered first in the sequence of forms occupies the 37th rank! Agreement can hardly be expected to prevail so far down the list. There also remains the looming possibility that forms of uncertain sign may have been labeled positive by Ungemach himself—this would explain the avalanche of positive forms!

The modified list of forms does not make any distinction between complementary diploids, {*hkl*} and {*hlk*}, the effect of the glide plane being restricted to faces perpendicular to it (one index equal to zero).

In conclusion, one should be well satisfied with the verification obtained, which is vastly better than any agreement could be if due to chance alone. A detailed morphological study of pyrite is, nevertheless, badly needed to confirm or ascertain the sign of the hemihedral forms.

The case of pyrite is a first example of space group determination, without the aid of *x*-rays, by means of the scantest morphological information, namely: isometric system (whatever the class); {001}, {111}, {012} dominant (regardless of relative importance). Among the 17 possible "morphological aspects" of the isometric system, only one gives

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relative importance of the forms by the size of the corresponding poles (the latter vary from tiny pencil points to circlets five millimeters in diameter).

Table 2. Pyrite

Space group $T_h^6 = Pa3$

| Bravais-Friedel Lattice *P* | Donnay-Harker Aspect *Pa3* | Comparison | | |
|---|---|---|---|---|
| | | B-F | Common | D-H |
| 001 | 111 | 001 | — | |
| 011 | 002 | 011 | — | |
| 111 | — 021 | | 111 | |
| 012=021 | 112 | | — | 002 |
| 112 | 022 | 012 — | — 021 | |
| 122 | 122 | | 112 | |
| *013=031 | 113 | | — | 022 |
| 113 | 023 — | | 122 | |
| 023=032 | 123=132 | *013=031 | — | |
| 123=132 | — 041⎫ | | 113 | |
| 014=041⎫ | 223⎭ | — 032 | 023 — | |
| 223⎭ | 114 | | 123=132 | |
| 114 | 133 | 014 — | — 041⎫ | |
| 133 | 024 — | | 223⎭ | |
| 124=142 | 124=142 | | 114 | |
| 233 | 233 | | 133 | |
| 034=043 | — 043 | | — | 024 — |
| *015=051⎫ | 134=143 | | 124=142 | |
| 134=143⎭ | 115 | | 233 | |
| 115 | 025 —⎫ | 034 — | — 043 | |
| 025=052⎫ | 234=243⎭ | *015=051 | —⎫ | |
| 234=243⎭ | *125=152 | | 134=143⎭ | |
| *125=152 | 144⎫ | | 115 | |
| 144⎫ | 225⎭ | — 052 | 025 —⎫ | |
| 225⎭ | 334 | | 234=243⎭ | |
| *035=053⎫ | *135=153 | | *125=152 | |
| 334⎭ | — 061 | | 144⎫ | |
| *135=153 | 116⎫ | | 225⎭ | |
| *016=061 | 235=253⎭ | *035=053 | —⎫ | |
| 116⎫ | *026=062 | | 334⎭ | |
| 235=253⎭ | *126=162⎫ | | *135=153 | |
| *126=162⎫ | 045 —⎬ | *016 — | — 061 | |
| 045=054⎬ | 344⎭ | | 116⎫ | |
| 344⎭ | *145=154 | | 235=253⎭ | |
| *145=154 | 335 | | — | *026=062 |
| 335 | *245=254 | | *126=162⎫ | |
| *245=254 | 136=163 | — 054 | 045 —⎬ | |
| 136=163 | ?236=263 | | 344⎭ | |
| ?236=263 | 345=354 | | *145=154 | |
| *017=071⎫ | 117⎫ | | 335 | |
| 345=354⎭ | * 155⎭ | | *245=154 | |
| 117⎫ | — 064 | | 136=163 | |
| *155⎭ | *027 | | ?236=263 | |

TABLE 2. (*Concluded*)

| Bravais-Friedel Lattice *P* | Donnay-Harker Aspect *Pa*3 | Comparison | | |
|---|---|---|---|---|
| | | B-F | Common | D-H |
| *027=072 | *146=164 | *017=071 | — | |
| *146=164 | *127=172 | | 345=354 | |
| *127=172 | 255 | | 117 | |
| 255 | 227 | | *155 | |
| | 445 | | — | — 064 |

N.B.—Unknown forms marked by asterisk (*), doubtful forms by query (?).

top ranks to the three dominant forms; to that aspect the space group *Pa*3 corresponds uniquely.

## SPACE GROUP DETERMINATION BY MORPHOLOGICAL CRITERIA

A "morphological aspect" corresponds to one or more space groups in a crystal system. Within a crystal class, however, a morphological aspect corresponds to one space group only (or, at the most, to two enantiomorphous space groups). Knowledge of the relative importance of the crystal forms usually suffices to limit the possible space groups to a very few, especially if the crystal class (point group) can be determined. Even if the crystal class is not known it is still possible, in certain favorable cases, to determine the space group uniquely. Pyrite is one example. Garnet is another. It will be given here as an illustration of the fact that the dominant form, in an isometric crystal, need not be the cube, the octahedron, or the rhombic dodecahedron, as demanded by the Law of Bravais and implied by the French nomenclature: hexahedral mode, octahedral mode, dodecahedral mode. Derivation of the 17 isometric "aspects" has shown that either one of these three forms can be dominant in all three lattice modes, except that the octahedron can never be dominant in the dodecahedral mode, where, however, the leucitohedron {112} can take first place.

*Examples: Garnet*, $Al_2Ca_3(SiO_4)_3$. Isomettic system. Hexoctahedral or holohedral class. ($O_h = 4/m\ \bar{3}\ 2/m$). $a_0 = 11.8$ A.U. Translation lattice, body centered (dodecahedral mode). Space group $O_h^{10} = Ia3d$. Here are the most salient morphological data, as given in Dana: the dodecahedron {011} and the trapezohedron {112} are the most common simple forms; the hexoctahedron {123} comes next; the cube {001} and the octahedron {111} are rare.

In order to account for the great importance of the leucitohedron {112} the Law of Bravais can only select the body centered lattice. This choice is confirmed by $x$-rays. Among the 17 isometric aspects only one gives top ranks to the three most important forms; this aspect uniquely determines the space group $Ia3d$.

Many discrepancies between the facts and the Bravais sequence are corrected by the new list (see Table 3, arranged like Table 1 for sulfur). The Bravais list expresses the condition that the sum of the indices must be even, which is imposed by the mode of the lattice. The new list takes into account the additional restrictions of the space group: $\{0kl\}$ with $k$ and $l$ even, $\{hhl\}$ with $2h+l=4n$. The cube, which came second, is now fourth. The octahedron, which was fifth, goes down to the fourteenth place. The leucitohedron comes first, followed immediately by the dodecahedron and the {123} hexoctahedron.

*Analcime*, NaAlSi$_2$O$_6$·H$_2$O. This mineral is selected as an example of a pseudo-symmetric species. The dominant "form" is, by far, the trapezohedron {112}, which often occurs alone. Other "forms" that have been observed: cube, dodecahedron, octahedron, tetrahexahedron {012}, and trisoctahedron {233}. Of these the octahedron is certainly the rarest. It is hard to assign relative importances to the remaining forms. The only combination given by Hintze that shows five forms (apparently the richest observed) may serve as an indication; its forms are, in order: 112.011.001.012.233. It was found at Friedensdorf, in Hessen.

TABLE 3. GARNET

Space group: $O_h^{10}=Ia3d$

| B-F | Com | D-H | B-F | Com | D-H | B-F | Com | D-H |
|---|---|---|---|---|---|---|---|---|
| 011 | — | | | 233 | | | 145 | |
| 002 | — | | *015 | — | | 226 | — | |
| | 112 | | | 134 | | | *136 | |
| | — | 022 | | *125 | | | — | 444 |
| 013 | — | | 035 | — | | *017 | — | |
| 222 | — | | 334 | — | | | *345 | |
| | 123 | | 244 | — | | | 046 | |
| | — | 004 | | *116 | | | *127 | |
| *114 | — | | | *235 | | | *255 | |
| | 024 | | | — | 026 | *037 | — | |

N.B.—Crystal forms that have not been observed on garnet are preceded by an asterisk (*).

Incomplete though the data may be, they can be accounted for by one of the morphological aspects only, the same as for garnet, namely: 112.022.123.004.024.233. · · · (octahedron coming 14th in the list). The fact that {123} has not been reported is an anomaly. It does not obscure the otherwise perfect agreement.

The pseudo-isometric character of the species being recognized, simple data on habit and form development permit one to predict that the symmetry of the structure will closely simulate that of the space group $O_h^{10}=Ia3d$. The results of the $x$-ray investigation have led to the recognition of a "pseudo-structure" ($S6_1$ type of *Strukturbericht*) based on a cubic cell ($a_0=13.7$ A.U.) and space group $O_h^{10}=Ia3d$. The confirmation is striking.

*Spinel*, $MgAl_2O_4$. The most typical feature of this species is the predominance of the octahedron. The dodecahedron and the trapezohedron {113} come next in importance. The cube never is a "habit form."

Out of the 17 isometric aspects four give {111} the first place. One is the aspect of pyrite, corresponding to the space group $T_h^6=Pa3$, with simple cubic lattice. This aspect is immediately eliminated as it gives the cube second rank, the dodecahedron fifth rank, and {113} seventh rank; not to mention its characteristic hemihedry. It would also demand the presence of {123}, which is unknown, as the first general form, whereas {135}, typical of the F lattice, is observed instead. The other three aspects are: (1) the Bravais list for an all-face centered lattice; (2) the same, slightly modified by symbolizing the cube {004} instead of {002} and making it retreat from second to fourth place; (3) the same list again, but further altered by the "extinction"[7] of all {$0kl$} forms for which the sum of the indices is not a multiple of 4.

The Bravais list is not as good as either one of its two modifications, on account of the rarity of the cube. The third list fits the facts better that the second, since neither {024} nor {046} are known, whereas {026} is observed. Comparison between the three aspects is shown in Table 4. The first aspect (headed "F" because it is the expression of the all-face centered lattice) corresponds to five space groups, one in each point group, namely: $T^2=F23$, $T_h^3=Fm3$, $T_d^2=F\bar{4}3m$, $O^3=F43$, $O_h^5=Fm3m$. The second aspect uniquely defines the space group $O^4=F4_13$. The third aspect is compatible with two space groups: $T_h^4=Fd3$ and $O_h^7=Fd3m$. We have seen that the form development points towards the last two space groups, even if the point group is unknown. Since the diploidal class can be ruled out, $Fd3m$ is the only possibility.

The $x$-ray results confirm the morphological conclusions. The röntgenographically possible space groups are given as $Fd3m$, $Fd3$, and $F4_13$, in *Strukturbericht*.

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[7] This use of the word "extinction," that recalls the correlated phenomenon in $x$-ray diffraction, may be found convenient. In the first and second lists, {012}, extinguished as such by the all-face centered lattice, appears as {024}. It is extinguished as {024} and occurs as {048} in the third list, owing to additional restrictions of the space group.

TABLE 4. SPINEL, $MgAl_2O_4$

| $F$ | $O^4$ | $T_h^5$, $O_h^7$ |
|---|---|---|
| 111 | 111 | 111 |
| 002 | — | — |
| 022 | 022 | 022 |
| 113 | 113 | 113 |
| — | 004 | 004 |
| 133 | 133 | 133 |
| *024 | *024 | — |
| 224 | — | 224 |
| *115 | — | *115 |
| 135 | — | 135 |
| 244 | same | 244 |
| 026 | as | 026 |
| *335 | list | *335 |
| *117 | F | *117 |
| *155 | — | *155 |
| *046 | — | — |
| *246 | — | *246 |

N.B.—Unknown forms are marked by an asterisk (*).

## PERSISTING ANOMALIES

Inasmuch as the law presented in this paper is of a strictly geometrical nature only, it cannot be expected to hold in all cases. Some anomalies do persist.

*Example: Halite*, NaCl. The space group is known to be $O_h^5 = Fm3m$. The translation lattice is all-face centered, the motif is composed of a sodium ion and a chlorine ion, one half of the cube edge apart (which explains why some authors describe the structure as composed of two "interpenetrating lattices"). In this case the Law of Bravais and the generalized law coincide (no screw axis, no glide plane). The new law is, therefore, just as powerless as the Law of Bravais. The anomalies shriek.

As a natural mineral, NaCl usually occurs in cubes. The other forms known are {011}, {111}, {012}, {123}. Artificially produced crystals show various habits according to the conditions of crystallization (the addition of urea to the solution produces octahedra, as is well known) and several new forms, the principal ones being {112} and {122}; the others, {014}, {034}, {035}, {045}, {233}, {345}. The cleavage, which is perfect, parallels the dominant habit form {001}. Only three of the 17 isometric aspects will give the cube the leading rank (see Table 5, first three columns): (1) the Bravais sequence for a simple cubic lattice (Table 5, first column, headed "*P*"); (2) the aspect that corresponds to the space groups $T_d^5$ and $O_h^6$, with an all-face centered lattice; (3) the aspect that corresponds to the space group $T_h^7$, with a body centered lattice. None of these is the one demanded by the law (fourth column, headed "*F*"). The best agreement is found in the "*P*" list. G. Friedel (1926, p. 144) had already stressed the anomaly. He pointed out that, if one did not discriminate between Na ions and Cl ions, the smallest cell would become simple cubic.

It is a curious fact that cadmium oxide CdO, which belongs to the same space group as NaCl and has the same structural type, does obey the law. The data given in Groth permit listing the forms as follows: {111}, dominant; {001} next; {011} third; and last a trapezohedron, which has not been measured, tentatively given in Groth (1906, p. 176) as {112}?. This list is in perfect agreement with the "*F*" sequence (see Table 5), even to the last form if the trapezohedron is {113}, which it may well be. Geometrical considerations are obviously insufficient to account for such cases. The reason why cadmium oxide conforms to the law whereas sodium chloride does not is probably to be sought in the less marked ionic character of the cadmium oxide structure.

TABLE 5. HALITE, NaCl

| *P* | $T_d^5$, $O_h^6$ | $T_h^7$ | *F* |
|---|---|---|---|
| 001 | 002 | 002 | 111 |
| 011 | 022 | 112 | 002 |
| 111 | 222 | 022 | 022 |
| 012 | 024 | 222 | *113 |
| 112 | *135 | 123 | *133 |
| — | 224 | *114 | 024 |
| 122 | 244 | 024 | 224 |
| *013 | *026 | *233 | *115 |
| *113 | *226 | *134 | *135 |
| *023 | *046 | *125 | 244 |
| 123 | 246 | *334 | *026 |
| — | *137 | 244 | *335 |
| 014 | 028 | *116 | *117 |
| *223 | *446 | *235 | *155 |

N.B.—Unknown forms are marked by an asterisk (*).

It has been shown above that, when the motif is composed of two "submotifs" enantiomorphous to each other or congruent but rotated with respect to each other, the reticular constant (reticular density, mesh area, or interplanar spacing) should be defined in terms of "equipoints" (representing "submotifs") instead of lattice nodes (standing for motifs) for all planes containing one kind of equipoints only (either lattice equipoints or space group equipoints). In the case of NaCl, on account of the ionic character of the structure, the motif may perhaps be thought of as composed of two "submotifs," one $Na^+$, the other $Cl^-$. Inasmuch as "submotifs" need not be in parallel orientation, it may perhaps be justified to enlarge the tolerance by supposing that ions of different nature can play the rôle of "submotifs." In the case of the sodium chloride structure, this hypothesis is particularly tempting; if the Na ions are imagined to lie at the nodes of the translation lattice, they can be considered as "lattice equipoints" while the Cl ions will become "space group equipoints." In such an hypothesis all the planes with indices all odd will have their spacing halved (or their mesh area doubled) and hence their indices multiplied by two. All other planes have their indices doubled already by virtue of the all-face centering of the lattice. The final result is thus to have all planes modified in the same manner, namely by doubling the indices, which means that the sequence of forms according to decreasing importance will be identical with that of a simple cubic lattice (the edge of the unit cube halved). All anomalies would then disappear.

We have shown that *the two-dimensional periodicity of a plane is the effective factor determining its morphological importance, regardless of what the motif of the mesh may be;* it need not be the same as the three-dimensional motif of the lattice, but may be a submotif thereof, *i.e.*, a part of the motif obtainable from the other parts by screw rotation or glide reflection. The working hypothesis introduced in interpreting the NaCl morphology is that the submotifs need not even be chemically identical.

## Summary

Independently of its theoretical justification the following law can be considered a law of observation, including the Law of Bravais as a particular case:

The morphological importance of a crystal face is inversely proportional to its reticular area $S$ if the lattice is of the hexahedral mode (no centering) and the space group is devoid of screw axes and glide planes. The effect of lattice centering, screw axes, and glide planes is corrected for if the face indices are replaced, in the $S$ formula, by the "multiple indices" of the lowest order of $x$-ray reflection compatible with the space group symmetry.

Many anomalies of the Law of Bravais are accounted for; some persist, since the law is purely geometrical, involving no physical consideration. The influence of space group symmetry is so preponderant, however, that it seldom becomes obscured by that of other factors. The law introduces a distinction between certain complementary merohedral

forms. It leads to the recognition of the various possible "morphological aspects" in any crystal system. The law determines the relative importance of the forms for a given space group; conversely the space group can be predicted from morphological features alone (without the help of $x$-ray methods).

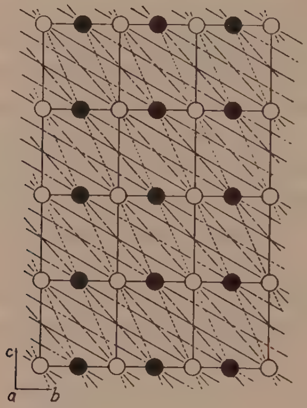

Fig. 1.

Orthorhombic Primitive Lattice.
Glide plane (100) parallel to plane of figure.
Systems of Points:—
Lattice equipoints: Open circles
Space group equipoints: Solid circles
The space group equipoints are mirror images of the lattice equipoints.
Systems of Planes:—
(021) - - - - - - - - - - - - - - - -
(011) Through lattice equipoints —— —— —— —— —— ——
(011) Through space group equipoints — – — – — – — – — – — –
(012) Through lattice equipoints ————————————————
(012) Through space group equipoints — – — – — – — – — – — – — –

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# THE PARAGENESIS AND COLOR OF FLUORITE IN THE ENGLISH PENNINES

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## CONTENTS

Introduction........ 468
Outline of the Geology of the Pennines........ 468
Paragenesis of Fluorite........ 470
  In Banded Veins........ 472
  In "Flats" and Cavities........ 473
Epimorphs after Fluorite........ 474
  In the Oxidation Zone........ 475
  In Primary Deposits........ 475
Distribution of Colored Fluorite in the Northern Pennines........ 476
Review of other Fluorite Occurrences........ 476
References........ 477

## INTRODUCTION

The beautiful violet crystals of fluorite from the English Pennines are known to mineral collectors the world over, being among the finest specimens of the mineral obtainable. There are few mineralogical museums in which examples bearing the labels "Cumberland," "Durham," "Weardale" or "Boltsburn" are not to be found. "Blue John," the deep purple and yellow banded fibrous variety of the mineral, which was first used by the Romans for the making of ornaments, also comes from this region. The details of mode of occurrence of fluorite in the Pennines are not as familiar to the mineralogist as are the specimens. Encouraged, therefore, by a suggestion made by Professor Palache some years ago, the present paper has been prepared. Boltsburn mine, for many years the source of some of the finest specimens, closed down in 1931 and is now flooded. It seems desirable to place on record an account of its cavities. The results of a study of the distribution of colored varieties of fluorite in the Northern Pennines, demonstrating the existence of regional color-zones, are also presented for the first time.

## OUTLINE OF THE GEOLOGY OF THE PENNINES

The Pennine Range extends from the valley of the South Tyne, west of Newcastle, to Central Derbyshire. It is made up of flat-lying or gently folded Carboniferous sedimentary rocks, pierced in places by minor intrusions, resting on a basement of strongly folded Lower Palaeozoics. The northern part of the area, between the Tyne and the Craven district of West Yorkshire, is a structural block bounded on the west, north and south by major faults. Lower Carboniferous rocks outcrop over the high western part of the block, and in general dip to the east, disappear-ing eventually beneath the coalfields of Durham and Yorkshire. The general easterly dip seems to have been superimposed on two gentle domes, occupying respectively the northern and southern halves of the block, separated by a sharp east-west syncline at Stainmoor. The Lower Carboniferous succession here is made up of massive limestones, overlain by alternating thin limestones, sandstones and shales (the Yoredale series). The limestone bands in the latter series are persistent, but the shales and sandstones are subject to considerable variation. The Great limestone, 60 feet thick, which is the thickest of the Yoredale limestones in the northern part of the block, is important because it has proved a very favourable horizon for mineralisation.

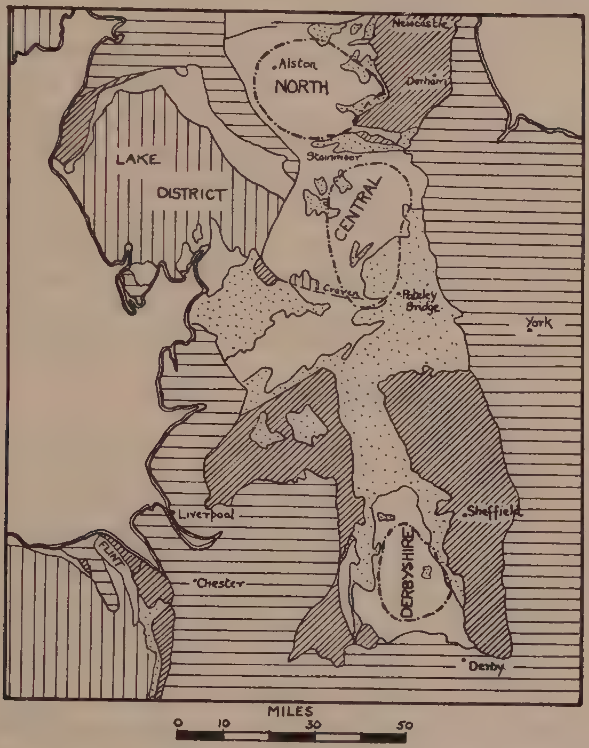

FIG. 1. Sketch map of Northern England. Unshaded areas, Lower Carboniferous; Stipple, Millstone Grit. Diagonal shading, Coal Measures. Vertical shading, Pre-Carboniferous rocks. Horizontal shading, Post-Carboniferous rocks. Heavy broken lines show the limits of the mineralised areas of the Pennines. Geological boundaries from Teall's Geological Map of the British Isles (2nd ed. 1912).

South of the Craven faults the Lower Carboniferous rocks are covered by Millstone Grit. They re-appear, however, in the High Peak district of Derbyshire, where a broad anticline brings to the surface shale and sandstone equivalent to the Yoredale series of the northern districts, and underlying massive limestone 1500 feet thick.

North of Stainmoor there are two suites of minor intrusions. The well-known Whin Sill, actually a series of sills at different horizons in the Carboniferous limestone series, is of late Carboniferous age. The rock is a quartz dolerite. Associated dikes strike east-north-east. A series of tholeiite dikes, associated with the Tertiary igneous activity of Western Scotland, strike west-north-west across the area in linear echelons.

In Derbyshire there are basaltic lavas interbedded with the limestone, and intrusive dolerite sills and agglomerate and basaltic necks.

Lead, zinc and copper ores, barite and witherite as well as fluorite have been mined in the Pennines. The deposits are confined for all practical purposes to the Lower Carboniferous rocks. There are three mineralised districts (Fig. 1); the North Pennine field, the Central Pennine field, and the Derbyshire field. The deposits occur as veins along fault-fissures of small displacement; along mineralised joints; in caverns, pipes, and metasomatic replacements ("flats"). The veins are very numerous, some 584 being known in the Northern field alone.

## Paragenesis of Fluorite

The quantitatively important primary minerals in the deposits include galena, sphalerite, fluorite, barite, witherite and calcite. Any one of these may constitute the bulk of an individual deposit. In addition, the following minerals occur in subordinate amounts: chalcopyrite, jamesonite, marcasite, pyrite, niccolite, ullmannite, quartz, chalcedony, aragonite, siderite, dolomite, alstonite, baryto-calcite, strontianite. In the North Pennine field, where the necessary detailed study has been made, it has been shown (1934) that the minerals are distributed in a rational manner, in concentric regional zones. Here a fluorite zone occupying the veins of the central part of the area is surrounded by an outer zone of barium minerals (Fig. 2). There is a corresponding arrangement of sulphides, and in the central area, the fluorite occurs as gangue in veins belonging to the copper and lead-zinc zones. The quantity of fluorite greatly exceeds that of sulphides in the innermost part of the central area, and the veins are wrought for their fluorspar.

There are indications that a similar zonal arrangement exists in Derbyshire (Webb and Drabble, 1908; Sweet, 1930). Veins with fluorite occupy the eastern side of the field, and it seems likely that much of the fluorite zone is still concealed beneath the shales covering the Carboniferous limestone. To the west, the fluorite zone gives place to barite, as in the northern area. The barite zone is succeeded by a calcite zone.

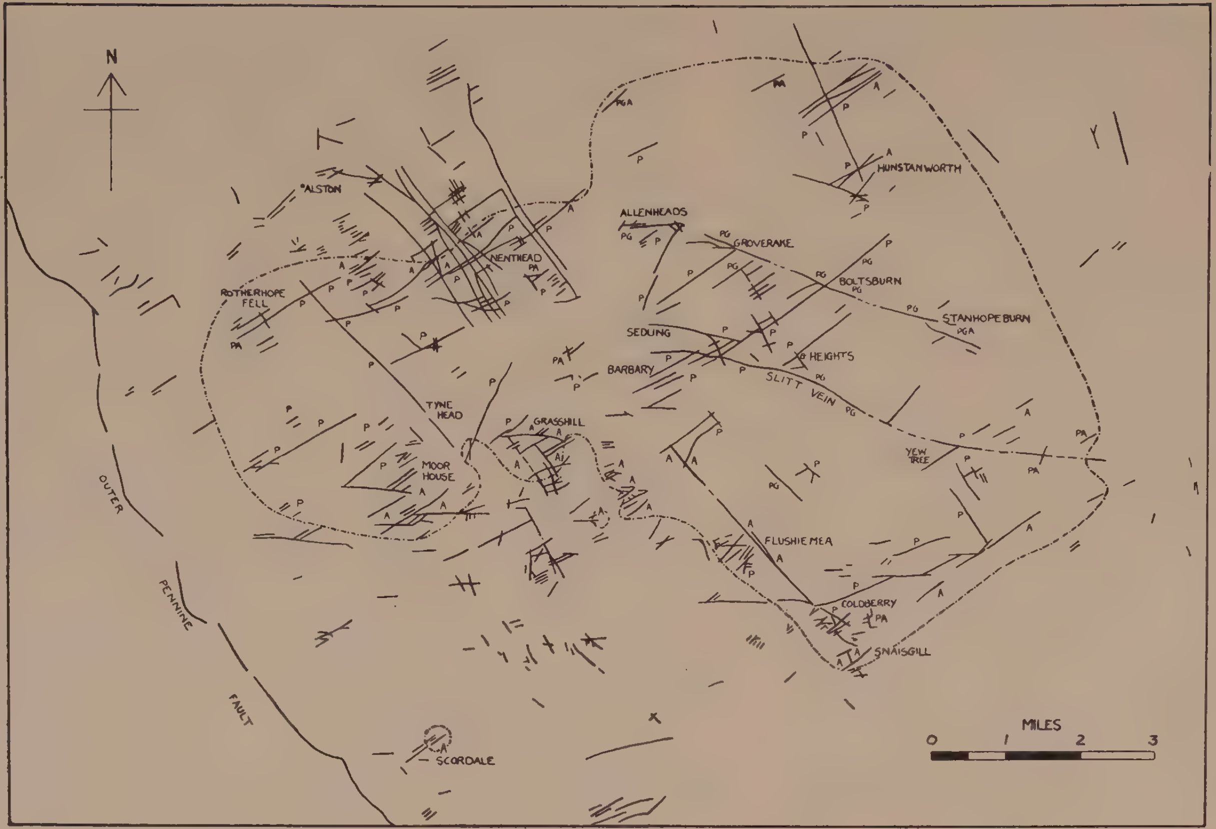

FIG. 2. Distribution of colored fluroite in the North Pennine area. Continuous lines, veins and faults. The broken line indicates the margin of the fluorite zone, which is surrounded by the barite zone. P, purple; G, green; A, amber.

Fluorite also occurs in the Central Pennine field, but the details of its distribution have not yet been worked out.

The mineralogy of the fluorite from the Pennines is so well known that it is only necessary to mention that isometric penetration twins are the only important morphological type. The edges of the cube faces are often beveled by a tetrahexahedron, probably {310}, and vicinal faces, indicated by stria, are almost always present on the cube faces through which the penetration twins emerge. The octahedral variety is very rare and I have never had the good fortune to find an example.

The relations between fluorite and its associated minerals will be considered according to the two chief modes of occurrence of deposits.

*In Banded Veins.* Banded structure, sometimes rudimentary, sometimes very well developed with many repetitions, is characteristic of the veins of the region. The bands seldom exhibit a simple sequence of minerals, for each mineral present in the vein may be repeated several times. It follows that there is no such thing as a simple "order of deposition."

The remarkable fact about the banding is that it shows that the veins were filled by successive incrustations of pure minerals, both walls of the vein being covered simultaneously. The symmetrical development of bands indicates that they are due in general to simple deposition, not to re-fracturing and replacement; and evidence of reopening is rare and of little importance. Individual pure bands may vary from less than an inch to several feet in width. The bands themselves are not always continuous; sulphides in fluorite veins frequently occur as a series of isolated masses within the gangue. Inspection usually reveals however that these are aligned parallel to the banding, and joined up by a discontinuity in the fluorite. Such isolated masses must therefore be regarded as incompletely developed bands.

Crystal faces may or may not occur on the inward-facing surface of a band. Some typical examples will illustrate this point. The vein at Sedling mine showed, from wall to centre, bands as follows: sphalerite—massive mauve fluorite—quartz—fluorite—galena—fluorite—cavities with quartz and green fluorite crystals. Here crystal faces were to be found in the centre of the vein only. A narrow vein at Groverake showed: purple fluorite—chalcedony—galena—chalcedony—green fluorite with good faces —quartz with good faces. A vein at Whiteheaps mine, Hunstanworth, showed six alternations of fluorite and quartz, good faces being developed on the inward surface of each fluorite band. It is easier to picture the conditions obtaining when crystal faces are developed than those which inhibit their free growth. In any case, the details of the process are not yet understood.

Of more fundamental interest is the problem of the cause of the banding. The explanation probably lies in the nature and flow of the mineralising solutions. If these were electrolytic solutions, then their composition must have been subject to repeated change, and they must in general have been saturated with respect to only one solute at once. If colloidal, then some process must be imagined whereby only one disperse phase is caused to coagulate at any one time. A possible mechanism is the "plating-out" process, applied to these veins a century ago by Leithart (1838). The essential points are summarised in the following quotation:

> Suppose the rocks forming the walls of a vein be electrified negatively, in this case they will attract to them the electro-positive elements of matter, as the metals, etc.; but when these electropositive elements are accumulated on the walls to some certain thickness, the action of the wall-rock will become null, and the positively polarising substance plating the walls will act as electro-positive surfaces, and attract to them . . . the electro-negative elements, as oxygen, fluorine, etc.; or the substances in which they predominate, as quartz, fluate of lime etc.; these alternations being repeated until the vein is filled up, if the electrical action continue (1838, pp. 49, 50).

A similar mechanism has been advocated for the coagulation of disperse phases in colloidal solution by Boydell (1927). Colloidal solutions may have been developed during the formation of the veins here under discussion, and cryptocrystalline varieties of silica may have been deposited from them; but in the main, the massive vein deposits were probably deposited from electrolytic solutions. Perhaps a combination of changing composition and "plating-out" is the explanation of the banded texture.

Certain minerals tend to appear only in the outer bands in the veins. These include chalcopyrite, marcasite and usually sphalerite. In complex veins, barite and calcite often occur in the inner bands only. In the North Pennine area, examination of a large number of specimens failed to reveal a single case in which barite had crystallised earlier than fluorite; but interbanding of fluorite and barite has been observed at the Odin and Crich mines in Derbyshire.

*In "Flats" and Cavities.* The crystal-lined cavities found in replacement deposits, cavern deposits and pipes in limestone are the source of the finest fluorite crystals. Compact replacement deposits are rare in the Pennines and in general, limestone dissolved has exceeded new material deposited in amount. Indeed, in certain deposits the first effect of the mineralising solutions seems to have been the wholesale solution of limestone, forming caverns; minerals were later deposited on the floor, walls and roof. Cavern deposits are found in Derbyshire and the Central field. In the thin limestones of the northern area, deposition more nearly kept pace with solution and the cavities are smaller.

At the Boltsburn mine, cavities were found in "flat" deposits which occurred on both sides of a fissure vein. Immediately adjacent to the vein was a belt of compact limestone, recrystallised and replaced by siderite and dolomite. Beyond this lay mineralised ground rich in galena, with fluorite, quartz and siderite as the principal gangue minerals. Irregular cavities up to 50 feet long and only a few feet high were encountered in this belt, completely lined with crystals. Fluorite in partly developed cubes as much as 15 inches on the side were observed, but inspection showed these to be composed of many smaller cubes in polysynthetic growth. Complete cubes up to 6 inches side with penetration twinning were not uncommon, and were picked out for use in optical work.

Detailed examination showed that in these cavities crustification for more complex than that in the banded veins was present. A typical example of the sequence of crusts is as follows: green fluorite—sphalerite—colorless fluorite—chalcedony—colorless fluorite—dolomite—galena—quartz—calcite. In the cavities, it is the general rule that crystal faces have developed at each incrustation. Examination of a large number of cavities failed to reveal any consistent order of deposition of minerals, or even any consistent repetition in the sequence. Why should the minerals separate in pure crusts, instead of in a thoroughly mixed granular mass? Only laboratory investigation of precipitation from complex solutions is likely to solve this problem.

Stalactites composed of the primary minerals of the deposits were observed in the cavities at Boltsburn and elsewhere. Such occurrences are sufficiently rare among mineral deposits to make them worthy of special mention. Interesting examples composed of siderite covered with crystals of fluorite and galena, which were found in West level, Boltsburn, had apparently grown upwards. As they have a central tubular hole through which the solutions passed they must be classed as stalactites and not stalagmites. Beautiful stalactites made up of crystals of purple fluorite and quartz, sometimes in several layers, were formerly obtainable at Boltsburn. Slender stalactites composed of "nail head" calcite crystals were also found here. Sphalerite stalactites, composed of radiating crystals, were obtainable from a vein at Hunstanworth.

## Epimorphs After Fluorite

Casts of fluorite crystals preserved in minerals which formerly covered them are occasionally found in the deposits. The term "epimorph" seems to be a suitable one to apply to such "negative crystals," preserving as they do surface impressions of minerals no longer present. Fluorite epimorphs originated in three different ways in the present area.

*In the Oxidation Zone.* Epimorphs often occur in the outcrops of the deposits. Here they are due to the removal of fluorite mechanically and chemically, leaving impressions in such stable minerals as quartz and chalcedony. That chemical solution of fluorite occurs in the oxidation zone is evident from an examination of natural surfaces of fluorite crystals from this zone under the reflecting microscope, which reveals innumerable tiny etch pits. Such etching is everywhere to be seen in the oxidation zone, but it is very rare below this zone. It should be noted that the solution of fluorite is a much slower process than the other chemical processes in the oxidation zone, so that substantial quantities of the mineral persist in this zone.

Dr. J. A. Smythe undertook a laboratory investigation of the etching of fluorite collected during the present study, and the following results are quoted by his kind permission:

> The surface were deeply etched by immersion in 5% HCl and 5% $H_2SO_4$ on the water bath for 10 hours, at about 83°C. 5% $Na_2CO_3$ and 5% KOH under similar conditions produced very much less notable results. In the cold, the same acids produced etching after immersion of the surface in them for three days; slight etching was produced by $Na_2CO_3$. HF had no effect.

These results are of interest because they suggest that the etching in the oxidation zone is due more to the presence of sulphuric acid than to the action of carbonates in solution. Natural and artificial etch pits are square in shape, oriented at 45° to the edges of the cube.

*In Primary Deposits.* In deposits beyond the reach of the circulating waters of the oxidation zone, epimorphs after fluorite are also occasionally found. The origin of some of these appears to be purely mechanical. Crusts of other minerals, which have covered fluorite crystals on the roofs of cavities, have fallen down, perhaps shaken by slight earth tremors. Some shaking-down of crystals from the roofs of cavities at Boltsburn seems to have occurred during the late stages of the mineralisation there, and a generation of huge calcite crystals followed the event, cementing together the fragments on the floor. No other primary minerals were deposited after the fall.

This explanation is, however, inadequate to cover all the observed cases. Professor Palache has pointed out to me specimens from this area in the Harvard collection which from their shape and from the presence of epimorphs on both sides could not have been formed in this way. These, therefore, imply a primary resorption of fluorite during the mineralisation process. Evidence of primary resorption of marcasite was found at the Nentsberry mine, near Nenthead, where epimorphs after marcasite occur.

## DISTRIBUTION OF COLORED FLUORITE IN THE NORTHERN PENNINES

During the investigation of the distribution of primary minerals in the North Pennine area, which led to the establishment of the zonal arrangement (Dunham, 1934), note was made of the color of the fluorite whenever that mineral was recorded. Plotting of the results on a map showed that just as there is a systematic distribution of minerals in the area, there is also a systematic distribution of colored varieties of fluorite.

Massive fluorite in the veins is generally white and opaque, or slightly tinted with mauve or green. Crystals, however, show a variety of beautiful tints, among which purple and amber are the commonest, green somewhat less common. In the central part of the fluorite zone, the crystals are purple or occasionally green. In the outer part of the zone, these give place to amber varieties (Fig. 2). The approaching transition from fluorite to barite in the veins is thus heralded by the appearance of amber fluorite. It was noteworthy that in every locality where barite and fluorite were found together, the color of the fluorite was amber. Scordale, Flushiemea, Snaisgill and Grasshill are the most notable of these localities.

However, the cause of the color cannot be chemically related to barite, for elsewhere purple and green fluorite are found in intimate association with barite, as in Derbyshire. Thus the only conclusion that can justifiably be drawn is that the purple and green varities crystallised at a higher temperature than the amber variety. Any conclusion about the cause of the color of fluorite based on chemical evidence must account for this relation, established with surprising clearness in the present area.

It should be noted that Smythe (1927) had observed the association of amber fluorite and barite some years before the present work.

Some interesting specimens from the Rotherhope Fell mine show that the amber variety crystallised later than the purple; individual crystals here have purple coloration inside, and amber margins. At the Blue John mine in Derbyshire, the upper and under surfaces of flat "veins" are coated with deep blue or purple fluorite, while the space between these is filled with clay, yellow fluorite crystals, and nodular barite (Carruthers and Pocock, 1922).

## REVIEW OF OTHER FLUORITE OCCURRENCES

A search of the literature was made in the hope of finding other cases in which the relation of purple and amber varieties of fluorite had been established. None was found, however, no doubt because the necessary detailed observations have not been made. Some brief general conclusions about the typical mineral associated of fluorite may be appropriate.

The paragenesis here described is one which is found in all parts of the world, and it is noteworthy that all the deposits which are worked commercially for that mineral show an essentially similar mineral assemblage. The deposits of Illinois and Kentucky have many features in common with those of the Pennines. Barite figures prominently in the list of minerals; galena and sphalerite also occur (Ulrich, 1901; Bain, 1905). In New Mexico quartz, calcite, barite and the simple base-metal sulphides and their oxidation products are associated with fluorite in a great variety of different country rocks (Johnston, 1928; Dunham, 1935). Green fluorite seems to be the commonest variety in this state. A similar assemblage is to be found in the commercial deposits throughout the Western United States (Burchard, 1933). The same assemblage appears in the Massif Central of France (Chermette and Sire, 1935), in the Harz, Thuringia, Saxony, the Sudetes, the Bayrische Oberpfalz, and the Schwartzwald (Medenbach, 1934). In South Africa, the deposits of the Western Transvaal are essentially similar (Kupferburger, 1928).

All these occurrences are of a relatively low temperature type. The presence of cavities indicates that they were not formed at great depths below the surface. They may be classed as leptothermal or in some cases as telethermal deposits, according to Graton's modification of the Lindgren classification (Graton, 1933).

In less important amounts, fluorite has a wide distribution among mineral deposits. It is a characteristic mineral of some epithermal deposits in volcanic rocks, as at Cripple Creek, Colo. In mesothermal as-assemblages it is to be found associated with copper deposits, as in Cornwall, where it generally dies out before the tin zone is reached (Dewey, 1925). Among high temperature deposits, it is restricted to those of the pyrometasomatic class, where it probably occurs as a late mineral, deposited when the temperature was falling rapidly. Finally some reference must be made to its association with "alkaline" igneous rocks, to which Lindgren (1933) attaches great importance. This association is particularly common in provinces of the "Fen" type.

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# CARMINITE AND ASSOCIATED MINERALS FROM MAPIMI, MEXICO[1]

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The mineral carminite was first described from the Luise Mine, at Horhausen, near Neuweid, Rhineland, Germany, but the amount of material available for investigation was so meager that the data are unsatisfactory. Carminite has also been reported from Cornwall, England, and Mt. Magnet, Tasmania. The so-called "red olivenite" from Tintic, Utah, found in many collections is carminite. A specimen in the U. S. National Museum from an unknown locality in Colorado also proves to be carminite.

The carminite and associated minerals from Mapimi, Durango, Mexico, were collected on a small dump near the North Shaft of the Ojuela Mine, in the summer of 1927 by Dr. Harry Berman and the writer during a season in the field under the auspices of the Holden Fund of the Harvard Mineralogical Museum, and the U. S. National Museum. The material consisted of blocks of massive to crystalline scorodite containing seams and pockets of arseniosiderite and small areas of dussertite and carminite.

The ores of the Ojuela Mine are replacement deposits in limestone and consist of galena, blende, pyrite and arsenopyrite in a matrix of quartz, dolomite and fluorite. Arsenopyrite is abundant, in some cases forming considerable bodies of sulfides. The oxidized ores are characterized by an abundance of arsenates, largely mimetite, together with wulfenite and the more ordinary oxide ore minerals.

## Carminite

The carminite occurs in minute crystals, less than one half mm. in length in cavities in either scorodite or arseniosiderite. They are dark carmine red in color and highly lustrous. It also forms heavy masses, with radiated structure, rather intimately mixed with cerussite, anglesite and plumbojarosite. It is almost always intimately associated with arseniosiderite and dussertite and is the rarest of the arsenates in the association.

*Chemical Properties.* The original chemical analysis of carminite by R. Müller was made on but 0.068 grams of material and the results are therefore unreliable and prove to be much in error. A reasonably pure sample of the Mapimi carminite was obtained, estimated to contain not more than 5% of impurities, largely cerussite. Analysis of this material, together with an analysis of the Colorado carminite and the theoretical composition for the formula accepted is given below.

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[1] Published with the permission of the Secretary of the Smithsonian Institution.

TABLE 1. CARMINITE: ANALYSES FROM MEXICO AND COLORADO

| | Mexico | Ratios | Colorado | Ratios | Theory |
|---|---|---|---|---|---|
| PbO | 37.30 | .1675 | 36.57 | .1633 | 35.38 |
| CaO | 0.44 | .0078 | 0.06 | .0011 | |
| MgO | 0.06 | .0015 | 0.02 | .0005 | |
| FeO | 0.21 | .0029 | 0.14 | | |
| $Fe_2O_3$ | 23.43 | .1467 | 23.81 | .1491 | 25.33 |
| $Al_2O_3$ | 0.96 | .0094 | 0.43 | .0042 | |
| $As_2O_5$ | 33.98 | .1426 | 34.49 | .1500 | 36.44 |
| $P_2O_5$ | | | | | |
| $H_2O+$ | 2.9 | .1687 | 3.13 | .1687 | 2.85 |
| $H_2O-$ | 0.10 | | | | |
| Insol. | 0.58 | | 0.46 | | |
| | 99.96 | | 99.11 | | 100.00 |

These analyses lead to the formula $PbO \cdot Fe_2O_3 \cdot As_2O_5 \cdot H_2O$, which may also be written $2FeAsO_4 \cdot Pb\,(OH)_2$. This is very much simpler than the formula $Pb_3As_2O_8 \cdot 10Fe\,AsO_4$, given by Dana and based on the old analysis of Müller.

The mineral is slowly soluble in hydrochloric acid with the separation of lead chloride. Before the blowpipe the mineral fuses easily with intumescence, coloring the flame pale blue. The bead obtained is lustrous black and not magnetic. In a closed tube it fuses, turns dark brown in color, and evolves a small amount of water.

*Cyrstallography.* The crystals of carminite are very small, measurable crystals not exceeding a millimeter. They are flattened parallel to the brachypinacoid, the faces of the unit prism and the brachydome being narrow. There is also a decided tendency of the crystals to group themselves in flat sheaf-like forms so that most of the larger crystals were unsuited for measurement. Further, the faces, especially those of the brachydome, are somewhat etched and hence rather dull. A larger number of crystals were mounted and examined for measurement but only five gave signals sufficiently distinct to be usable in the calculation of the elements. These measurements are given below.

TABLE 2. CARMINITE

Measurements of *m* (110)

| Crystal No. | Reflection | $\phi$ measured |
|---|---|---|
| 1 | Faint | 54°03′ |
| 1 | Faint | 52 43 |
| 1 | Good | 54 11 |
| 2 | Good | 53 46 |
| 2 | Faint | 53 52 |
| 4 | Faint | 53 30 |
| 4 | Faint | 53 25 |
| 4 | Good | 53 37 |
| 4 | Faint | 53 09 |
| 5 | Poor | 53 42 |
| 5 | Poor | 53 40 |
|  |  | Average 53°36′ |

Measurements of *e* (011)

| Crystal No. | Reflection | $\rho$ measured |
|---|---|---|
| 1 | Poor | 25°06′ |
| 2 | Fair | 24 52 |
| 2 | Fair | 24 33 |
| 3 | Good | 25 28 |
| 4 | Fair | 24 47 |
| 4 | Good | 24 32 |
| 5 | Faint | 25 15 |
| 5 | Faint | 25 15 |
|  |  | Average 25°00′ |

From these measurements the following elements have been calculated and the angle table prepared.

TABLE 3. CARMINITE, MAPIMI, DURANGO, MEXICO

Orthorhombic

$p_0=0.6325$ $q_0=0.4663$ $a=0.7373$ $c=0.4663$

|  | Müller | Gdt. | $\phi$ | $\rho$ | No. faces | Limits |
|---|---|---|---|---|---|---|
| *o* | 010 | $0\infty$ | 0 | 90°00′ | 8 | — |
| *m* | 110 | $\infty$ | 53°36′ | 90 00 | 11 | 52°43 –54°11′ |
| *e* | 011 | 01 | 0 | 25 00 | 8 | 24 32 –25 28 |

In habit the crystals of carminite are lath-like, prismatic and flattened to the brachypinacoid (010). As already stated there is a tendency for the crystals to be aggregated into sheaf-like forms, and acicular radiated groups are also commonly found. Where doubly terminated crystals are found both ends are equally well developed and show no evidence of hemimorphism.

*Optical Properties.*[2] The color of carminite is dark carmine red. Under the microscope the pleochroism is strong, $X$=pale yellowish red, $Y$ and $Z$=dark carmine red. Absorption $Y$ and $Z>X$. Biaxial, positive, with $2V$ moderately large. Dispersion strong $r<v$. Extinction parallel; elongation negative. Birefringence low; $\alpha=2.070$, $\beta=2.070$, $\gamma=2.080$. The cleavage is perfect.

## SCORODITE

The scorodite forms large masses and constitute the main bulk of all the specimens collected. Two forms were found; one in coarse granular masses with numerous small vugs of crystals of a clean gray-green color, and the other in rounded concretionary masses of compact material lighter in color and abundantly veined by brown arseniosiderite, or with pockets and cavities of carminite and dussertite.

The crystals of scorodite are simple in habit, consisting of the pyramid *p* (111) only slightly modified by *a* (100) and small triangular faces of *d* (120), so that the crystals have an almost simple "octahedral" habit. An analysis of selected crystals gave the composition given below.

ANALYSIS OF SCORODITE FROM MAPIMI, MEXICO

F. A. Gonyer, *Analyst*

| | |
|---|---|
| Insol. | 0.12 |
| $As_2O_5$ | 48.96 |
| $Fe_2O_3$ | 34.20 |
| $Al_2O_3$ | 1.60 |
| CaO | 0.54 |
| MgO | 0.22 |
| $H_2O$ | 14.53 |
| | 100.17 |

This scorodite is biaxial, positive, with a medium optical axial angle. Dispersion is strong; $r>v$. The indices of refraction are $\alpha=1.787$, $\beta=1.795$, $\gamma=1.810$. It is, therefore, normal scorodite.

## ARSENIOSIDERITE

This mineral occurs as fine grained masses of light to dark chestnut brown color. It forms reticulating veinlets and replacement masses in the compact pale colored scorodite. It also forms purer masses of a darker color, in which original vugs of scorodite crystals have been completely altered to the arseniosiderite, yielding sharp pseudomorphs. This latter type usually carries small cavities lined with fine small carminite crystals and the entire mass is obviously derived from original scorodite.

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[2] Determined by Miss Jewell Glass.

The massive dark brown material was selected for analysis. Thin sections of this material showed it to be made up of a confused aggregate of crystals and that it carried a few small nests of carminite and perhaps some limonite. The following table gives the analysis, together with the molecular ratios and the theoretical composition for the formula accepted.

ARSENIOSIDERITE, MAPIMI, MEXICO

W. F. Foshag, *Analyst*

| | | | |
|---|---|---|---|
| $As_2O_5$ | 42.67 | .1778 | 43.6 |
| PbO | 0.28 | .0012 | |
| $Fe_2O_3$ | 32.71 | .2048 | 30.3 |
| FeO | 0.12 | .0016 | |
| CaO | 14.44 | .2574 | 15.9 |
| MgO | 0.61 | .0015 | |
| $H_2O$ | 9.34 | .5172 | 10.2 |
| Insol. | 0.40 | | |
| | 100.57 | | 100.0 |

Allowing for a small amount of carminite, the analysis yields reasonably well the formula: $3CaO \cdot 2Fe_2O_3 \cdot 2As_2O_5 \cdot 6H_2O$. An excess of iron, above that necessary for this formula may be ascribed to limonite. This is the formula given to mazapilite but differs from the usually accepted composition for arseniosiderite, based on the original Romanêche material.

## THE NATURE OF MAZAPILITE

Mazapilite was described by König (1889, pp. 85–88) as a new species from the Jesus Maria Mine, Mazapil Mining District, Zacatecas, Mexico. It occurs as well formed crystals embedded in calcite. Their color is deep chestnut brown, almost black and have a brownish red streak. While the crystals are sharp in form, thin sections show that they are not single crystals but a firm mass of interlocking grains. This suggests that they are probably pseudomorphous. The common occurrence of arseniosiderite as pseudomorphs after scorodite at Ojuela suggests that mazapilite is of this nature. A comparison of the crystal angles of mazapilite and scorodite leaves little doubt that this is actually the case.

TABLE 4. SCORODITE AND MAZAPILITE: CRYSTAL ANGLES

| Form | Scorodite | | Form | Mazapilite | |
|---|---|---|---|---|---|
| | $\phi$ | $\rho$ | | $\phi$ | $\rho$ |
| *a*(120) | 29°56′ | 90°00′ | *n*(120) | 30°03′ | 90°00′ |
| *p*(111) | 49 02 | 55 42 | *o*(111) | 49 10 | 56 30 |
| *n*(201) | 90 00 | 65 42 | *r*(201) | 90 00 | 66 23 |
| *e*(012) | 0 00 | 25 40 | *d*(012) | 0 00 | 26 17 |

Larsen (1921, p. 42), from a comparison of the optical properties of arseniosiderite and mazapilite, has already suggested their identity. Mazapilite is, then, arseniosiderite pseudomorphous after scorodite. Unfortunately, the material available is of such a nature that samples of unquestioned purity are not readily obtainable and it is difficult therefore to choose between several possible formulas for arseniosiderite. The more recent analysis suggests that the composition ascribed to "mazapilite" is the correct one for the species.

## DUSSERTITE

It was not possible to prepare a sample of this mineral sufficiently pure for analysis but in physical appearance, optical properties, and qualitative composition it is definitely dussertite.

The dussertite is always associated with the late minerals, carminite and arseniosiderite, and is not found in the scorodite without one or the other of these associates. It is fine granular in texture and has a clear pistachio green color, not unlike granular epidote. It is found either as a zone between carminite and scorodite, or is small, rounded masses in arseniosiderite. Crystals appear rhombohedral under the microscope.

*Optical Properties.*[3] Color deep chrysolite green (Ridegway). Uniaxial to abnormally biaxial with $2V=15°-20°$. Negative. $\epsilon=1.845$, $\omega=1.870$. Barth and Berman (1930, pp. 36–37) give for dussertite from the original locality, Djebel Debar, Algeria; uniaxial, negative. $\epsilon=1.85$, $\omega=1.87$; while Barthoux (1925) in his original description, gives its properties as uniaxial negative, with $n$ between 1.80 and 1.88. This is then the second recorded occurrence of dussertite.

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[3] Determined by Miss Jewell Glass.

# SILICATE-WATER SYSTEMS: THE "OSMOTIC PRESSURE" OF SILICATE MELTS

Roy W. Goranson, *Geophysical Laboratory, Washington, D.C.*

The problem of determining the solubility of water in silicate melts when the two phases are subjected to the same confining pressure has occupied the attention of the writer for some time; and results of his work have been published in two previous papers (1931, 1936). There is, however, another important aspect of this work that merits attention, namely the evaluation of the solubility when the hydrostatic pressure is not the same on the two phases, water and silicate solution. The second case, with which this paper is concerned, is important in problems associated with volcanism and certain other phases of igneous activity.

Differential hydrostatic pressure on silicate and water would occur if the country rock surrounding a magma were pervious to water and impervious to the silicate melt; for such a case the magma would be under a pressure equivalent to the overlying rock whereas the water would be at a pressure equivalent to its own head. Solution of this problem is then related to that of the phenomenon described as "osmotic pressure."

As ordinarily stated, however, osmotic pressure refers to a condition wherein the membrane separating the solvent and solution is permeable only to the solvent whereas for the problem here considered the membrane is assumed to be permeable only to the solute which in this problem is water. Solute is a term used to designate the more dilute component and solvent the more concentrated component of a solution. Ordinarily water is the solvent but here it is the more dilute phase, therefore the solute, and the silicate melt has the role of solvent.

The direct determination of the solubility relations under these conditions would be extremely difficult to carry out experimentally and has therefore been obtained from other thermodynamic properties of the system. As it does not seem to be generally understood that two equally valid expressions may be written for the osmotic pressure, with usage and "rigor" somewhat divided between the two expressions, the thermodynamic relations will be formulated *first* for the case where the membrane is permeable only to the solvent and *secondly* where it is permeable only to the solute.

The following statement of the phenomenon seems to be generally accepted as the definition of osmotic pressure and is applicable to our first case. If a vessel contains a solution, consisting of solvent (component 1) and solute (component 2), which is separated from the pure substance "1" by a membrane permeable only to substance "1," and both phases are at the same temperature and pressure, then the solution will tend to become more dilute by transference of solvent from the pure solvent phase. The increase in pressure that must be exerted on the solution in order to maintain equilibrium is called the osmotic pressure.

To conform with this statement let there be two phases, one of pure substance "1" and the other a solution of component "2" in "1," both at the same temperature but at different pressures such that they are in equilibrium with respect to component "1." Then the molar chemical potentials of "1" are the same in each phase or

$$\overline{F}_1(T,\ p,\ N_1) = F_1(T,\ p_0) \tag{1}$$

where $\overline{F}_1(T,\ p,\ N_1)$ denotes the molar chemical potential ($M_1\mu_1$) of "1" in the solution at temperature $T$, pressure $p$, and mol fraction $N_1$ of "1"; $F_1(T,\ p_0)$ denotes the free energy per mole ($\zeta/M_1$) of the pure substance "1" at $T$ and $p_0$.

If $F_1(T,\ p)$ be subtracted from both sides of equation (1) then

$$\begin{aligned}\overline{F}_1(T,\ p,\ N_1) - F_1(T,\ p) &= -\int_{p_0}^{p} v\,dp \\ &\doteq -[v](p-p_0) = -[v]\pi \qquad \text{(2a)}\end{aligned}$$

where $v$ denotes the molar volume of pure substance "1", the square brackets indicating a mean value of $v$ has been chosen for the pressure interval $p_0$ to $p$. ($T$, $p$, $N_1$) denotes the state in which the solution exists when in equilibrium with pure substance "1" at ($T$, $p_0$). The left hand side of the equation is equivalent to $RT \ln a_1(T,\ p,\ N_1)$ where $a_1$ is the activity of the solvent.

If $\overline{F}_1(T,\ p_0,\ N_1)$ be subtracted from each side of equation (1) then

$$\begin{aligned}\overline{F}_1(T,\ p_0,\ N_1) - F_1(T,\ p_0) &= -\int_{p_0}^{p} \bar{v}_1\,dp \\ &\doteq -[\bar{v}_1](p-p_0) = -[\bar{v}_1]\pi \qquad \text{(2b)}\end{aligned}$$

where $\bar{v}_1$ denotes the partial molar (fictive) volume of solvent in the solution; ($T$, $p_0$, $N_1$) denotes the state in which the solution would exist if the pressure $p$ were reduced to $p_0$, temperature and concentration remaining constant. The left hand side of (2b) is equivalent to $RT \ln a_1(T,\ p_0,\ N_1)$.

Here are then two different expressions for osmotic pressure which become identical only if the solution can be considered as ideal, for then (2a) becomes

$$RT \ln N_1 = -[v]\pi$$

and (2b) becomes

$$RT \ln N_1 = -[\bar{v}_1]\pi = -[v]\pi$$

because $v = \bar{v}_1$ for an ideal solution.

A very useful function introduced by Bjerrum is the osmotic coefficient $g = (\pi/\pi_{\text{ideal}})$, here

$$g = \frac{\bar{F}_1(T, p, N_1) - F_1(T, p)}{RT \ln N_1} = \frac{\ln a_1(T, p, N_1)}{\ln N_1},$$

or

$$g_0 = \frac{\bar{F}_1(T, p_0, N_1) - F_1(T, p_0)}{RT \ln N_1} = \frac{\ln a_1(T, p_0, N_1)}{\ln N_1},$$

and the two expressions for $g$ lose their identity unless it be specified to which of the two previous states $p$ or $p_0$ the solution is referred.

Lewis and Randall's (1923, p. 214) expression is equivalent to (2b); Donnan and Guggenheim (1932, p. 357) write the osmotic pressure as (2a). Guggenheim (1933, pp. 85, 109) writes two expressions which would apply for (2b) but as they are given under a heading of ideal solutions it would be immaterial which (2) he took as the expression; however, for a non-ideal solution he writes (1933, p. 120) $\pi = g(\pi_{\text{ideal}})$ in which $\pi$ seems to be a mixture of (2a) and (2b) because he writes $\bar{v}_1$ instead of $v$ and yet states that $g$ applies to the higher pressure $p$, which would not be correct. It is immaterial which expression be used provided the distinction in states be made because (2a) and (2b) are not in general equal.

The *second case* wherein the solute "2" is the permeable phase has, apparently, heretofore not received any attention; a similar treatment is also applicable here. For this second case we have, for equilibrium,

$$\bar{F}_2(T, p, N_2) = F_2(T, p_0) \tag{3}$$

where $p > p_0$, and $N_2$ denotes the mole fraction of solute (in this problem it is water). Then

$$\bar{F}_2(T, p, N_2) - \bar{F}_2(T, p, N_{2s}) = -\int_{p_0}^{p} v\, dp = -[v]\pi \tag{4a}$$

or

$$a_2(T, p, N_2)/a_2(T, p, N_{2s}) = \exp - \int_{p_0}^{p} \frac{v}{RT}\, dp \tag{4b}$$

where $a_2$ denotes the activity of the water in the solution, $v$ the molar volume of the water phase, and $(T, p, N_{2s})$ the state in which the solution would exist if in equilibrium with the water phase at $(T, p)$, i.e. $p_0 = p$. If the solution be ideal this expression reduces to

$$N_2/N_{2s} = \exp - \int_{p_0}^{p} \frac{v}{RT}\, dp \qquad (4c)$$

The expression corresponding to (2b) is of no interest to us here and is consequently omitted; to obtain it one need only substitute subscript 2 for 1, but there will be no corresponding activity function for this case. The treatment of these two cases is therefore very similar. In the first case, however, if $p \equiv p_0$ then the solution becomes more and more dilute by continual transference of phase 1 into the solution, whereas in the second case if $p \equiv p_0$ the transference of phase 2 into the solution continues only until the solution becomes saturated with respect to 2. Thus, in order to express the left hand sides of the equations for these two cases in terms of activities, their respective treatments must vary slightly to conform with the definitions of activity (Goranson, 1937).[1]

In order to evaluate expression (4) for a silicate melt and water it is necessary to know the $p$-$v$ isotherm for water at the temperature $T$ considered; furthermore, in order to express activity in terms of concentration, one must know the chemical potential of the water in the silicate solution as a function of the concentration.

The 1000°-isotherm of $v$ was plotted as a function of $p$ using the following data as a starting point: The data of Keenan and Keyes (1936) were used to obtain the $T$-$p$-$v$ relations of water at low pressures. The writer has made, at high pressures, a few rough measurements at 1000° C incidental to determining the feasibility of a method for obtaining $T$-$p$-$v$ data at high temperatures and pressures. From this plot $v\,dp$ was then integrated, analytically over some portions of the curve and graphically over other portions. These data were then expressed in terms of fugacity ratios and correlated with the activity ratios of the water in solution expressed in equation (4b). The relation of activity coefficient, and thus of activity, to concentration was obtained from experimentally determined solubility and freezing point data for the system albite-water. The data presented herein are therefore calculated for the system albite melt and water on the 1000° isotherm. The similarity in solubility relations of albite-water and granite-water systems would indicate an equivalent similarity here.

The data, presented in the following table and figure, have been calculated for confining pressures, $p$, on the silicate melt of 4000, 3000, and 2000 bars. The first column in the table expresses the pressure of the water phase and the second column expresses the hydrostatic pressure on the silicate solution minus that of the water phase, or osmotic pressure of the silicate solution for the corresponding concentration given in the third column as weight per cent of water in solution in the silicate melt.

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[1] The definition of activity is as adopted by the writer; for other definitions of activity these relations will be correspondingly altered.

TABLE 1. THE OSMOTIC PRESSURE (COLUMN 2) OF ALBITE-WATER SOLUTION IS GIVEN AS A FUNCTION OF WEIGHT PER CENT OF WATER IN SOLUTION (COLUMN 3) FOR DIFFERENT SILICATE SOLUTION PRESSURES, $p$ AT 1000°C.

| $p_0$ bars | $\pi = p - p_0$ | Wt. per cent of water in solution | Weight per cent of water in solution for $p = p_0$ |
|---|---|---|---|
| | $p=4000$ bars. $T=1000°$ | | |
| 4000 | 0 | 9.0 | 9.0 |
| 3500 | 500 | 5.6 | 8.7 |
| 3000 | 1000 | 3.8 | 8.3 |
| 2500 | 1500 | 2.8 | 8.0 |
| 2000 | 2000 | 2.0 | 7.4 |
| 1500 | 2500 | 1.4 | 6.6 |
| 1000 | 3000 | 0.84 | 5.5 |
| 500 | 3500 | 0.48 | 3.6 |
| | $p=3000$ bars. $T=1000°$ | | |
| 3000 | 0 | 8.3 | 8.3 |
| 2500 | 500 | 5.3 | 8.0 |
| 2000 | 1000 | 3.45 | 7.4 |
| 1500 | 1500 | 2.3 | 6.6 |
| 1000 | 2000 | 1.35 | 5.5 |
| 500 | 2500 | 0.64 | 3.6 |
| | $p=2000$ bars. $T=1000°$ | | |
| 2000 | 0 | 7.4 | 7.4 |
| 1500 | 500 | 4.4 | 6.6 |
| 1000 | 1000 | 2.5 | 5.5 |
| 500 | 1500 | 1.1 | 3.6 |

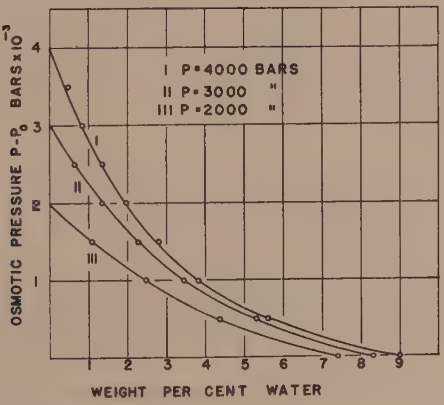

FIG. 1

Osmotic pressure, expressed as kilobars (bars $\times 10^{-3}$), is plotted as a function of the water concentration in the silicate (albite) melt, expressed as weight per cent, for three silicate melt pressures, namely 4, 3, and 2 kilobars (the corresponding curves being marked as I, II, and III respectively).

Columns 2 and 3 thus express the osmotic pressure of the silicate solution as a function of the water concentration. In the fourth column is given, for comparison, the weight per cent of water in solution in the silicate for the condition $p=p_0$, i.e. where the two phases are both at the same pressure $p_0$.

The concentrations given in column 3 are considerably less than the corresponding concentrations of column 4, and this fact may explain the rarity of rock glasses of high water content, and why rock glasses with a high water content behave differently on heating from those with a low water content. Dr. E. S. Shepherd has found that when rock glasses of high water content are heated the water begins to come off immediately and continues to come off as heating is continued; furthermore, for slow heating, the glass does not puff up appreciably. When glasses of low water content (1% or less) are heated no appreciable amount of water comes off until somewhere about 850° when the glass puffs up to many times its original size. Again, glasses of high water content are "perlitic" and not clear or clean-looking in texture as are those of low water content. The inference is that in these glasses of high water content the water is not in solution but exists as a separate phase which did not have time to diffuse out of the block and that the consequent unequal contraction of these two phases and resulting strains set up on cooling have caused the perlitic structure which is thus a fracture structure. Deposition of material from the water phase in these minute cracks and pores would give the glass its cloudy appearance.

It will also be evident from these figures that, if an impermeable rock mantle enclosing a silicate-water solution were to become permeable to water, for example by fissuring, permitting the water to escape, the energy available for explosive phenomena is considerably in excess of that previously indicated by the writer from a consideration only of the experimental solubility relations; here is also a possible mechanism for intermittent volcanic activity.

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# TECHNIQUE IN MINERALOGRAPHY AT HARVARD

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## CONTENTS

Introduction ........ 491
Preparation of the Specimen ........ 492
  Polishing ........ 492
  Abrasives ........ 495
  Mounting ........ 495
Microsampling ........ 497
Mineral Identification ........ 499
  General Treatises ........ 499
  Physical Properties ........ 500
    Hardness ........ 500
    Cleavage ........ 503
    Specific Gravity ........ 503
    Magnetism ........ 503
    Electrical Conductivity ........ 504
    *X*-Ray Analysis ........ 505
  Optical Properties ........ 505
    Color ........ 505
    Internal Reflection ........ 506
    Reflectivity ........ 507
    Polarization ........ 508
  Chemical Properties ........ 509
    Etch Tests ........ 509
    Microchemical Reactions ........ 510
    Spectrographic Analysis ........ 510
Microphotography ........ 511
Conclusion ........ 513
References ........ 515

## INTRODUCTION

Charles Palache's impress on the science of mineralogy, as other contributors to this Special Number doubtless will have emphasized, has come not alone because he is a lover of minerals and a master of their secrets; he has made mineralogy a living subject to the many his influence has reached, and this is largely because of his own keen interest in the *geological* aspects of mineral occurrence. In years of roaming through Western mining districts before I knew Palache, in repeated instances it was possible to recognize young mining engineers as Palache-trained because there would early emerge in one fashion or another their genuine feeling for minerals.

When the writer came to Harvard in 1909 to assist with the instruction in mining geology and began to pursue the microscopical study of ores in polished section by methods just then coming into use, Palache from the very first showed the most generous and sympathetic interest in this means of strengthening the mineralogy of the opaque minerals. And it is in large measure due to his unfailing encouragement, his wise counsel and the aid he has given in countless ways that a reasonably systematic attack has been maintained in the Laboratory of Mining Geology toward improved identification and a better understanding of the sulphides and related minerals.

It seems appropriate, therefore, that this Special Number intended to record examples of Palache's varied influences should contain a summary of the techniques and methods that have been developed with the aid of men who were his students and in an atmosphere pervaded by his inspiration. At the same time, opportunity is here afforded to respond to many requests that have come for description or discussion of mineralographic technique as employed at Harvard. In the following pages, attention is restricted to instrumental and manipulative procedure with the opaque minerals; no consideration is given to those operations chiefly dependent on transmitted light, nor to those more interpretative and philosophical phases of mineralography, such as textures, sequence, inversion, exsolution, genesis, deformation, alteration, etc., which more or less directly depend on the determinative steps here discussed.

## Preparation of the Specimen

### *Polishing*

In the paper by the late William Campbell (1906), which virtually ushered in the specialized microscopical study of opaque minerals by methods developed in metallography, relatively little emphasis was placed on the quality of polish to be given the materials for study. It became evident, however, that polishing methods suitable for such homogeneous and coherent substances as metals gave far less satisfactory results when applied to the varied mineral aggregations found in natural ores. It was finally concluded in this Laboratory that avoidance of the difficulties encountered, of which residual pits and scratches on the hard minerals and excessive relief between hard and soft minerals were dominant, could not be hoped for except by much lower pressures and slower speeds between specimen and lap, especially in early stages. Trial supported this idea, but indicated that the time required was thereby so greatly increased as to make hand-polishing impossible economically.

By 1920, therefore, a mechanical polisher had been designed and built to rotate ten appropriately mounted specimens under adjustable spring pressure against a counter-revolving lap, of cast iron for the grinding stage, and fabric-covered for the polishing stage. After several years of tantalizing encouragements that never reached satisfaction, during which N. Sabsay resourcefully tested one modification after another, it was decided to start anew.

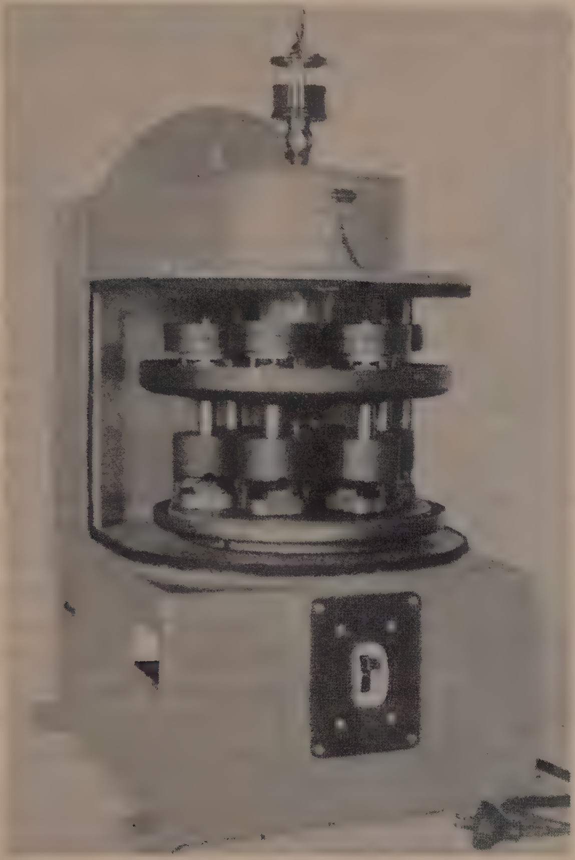

FIG. 1. Latest Model of Polishing Machine shown with transparent dust-proof doors removed.
(Courtesy of Mico Instrument Co.)

After an exhaustive review by J. W. Vanderwilt[1] of the literature on polishing and buffing in all sorts of industries, followed by trials of many methods and materials, it was decided that there could be no mastery of relief so long as fabric-covered laps should be used; and eventually the experimental work pointed definitely to laps of essentially non-yielding metal (soft lead) even for the final stages of polish. The resulting machine and method described by Vanderwilt (1928) have since been substantially perfected, the machine more than the method. In these improvements, as well as in many other of our instrumental problems, we have had the effective cooperation of D. W. Mann, instrument maker for the Department of Physics at Harvard, and the Mann Instrument Company[2] of Cambridge. The fifth and latest model of the polishing machine is shown in Fig. 1.

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[1] Now Chief Geol., Climax Molybdenum Co., Colorado.

The operation of polishing mechanically on metal laps is an art, not a fool-proof process. Its present state results from investigations by Drs. A. B. Yates,[3] H. J. Fraser,[4] and E. B. Dane, Jr.,[5] and from the accumulated experience and steady interest of C. S. Fletcher.[6] Adequate description of the process would exceed the space appropriate here. Suffice it to say that this method, while not yet perfect, produces a quality of polished surface that far excels anything yet produced on heterogeneous ores by hand polishing. None of us familiar with both types of polishing would now willingly work with fabric-polished preparations. The difference is not so much one of mere "shininess"; far more important is the greatly improved seeing permitted by the absence of the dark bands due to relief. It has been found that these previously-obscured contacts between hard and soft minerals are favored places for minute components of prime significance. For example, it is now possible to see plainly, as to color and shape, grains of gold embedded in pyrite even though these be so tiny that $3\times10^{10}$ such particles would be required to make one cent's worth. Since gold grains of much larger size would look only like black pits if the polishing were done on fabric-covered laps, it is not surprising that many have been disappointed in studying gold ores of moderate tenor under the microscope or have proposed weird explanations of the manner of occurrence of the gold shown by assay. Production of polished surfaces that are virtually optically plane, by reduction of maximum relief to about one half of a wavelength, has allowed the attainment of a precision and reliability in several of the procedures described hereafter that would have been utterly impossible on surfaces polished by the old methods. This is especially true for the determination of hardness, reflectivity, and color as well as for microphotography.

Our efforts to produce sections for simultaneous examination by both transmitted and reflected light have not been attended with the success which descriptions by others had led us to expect. J. H. Moses,[7] who handled these trials, resorted to innumerable devices to put a polish on a thin section or to thin a section already polished; but, despite use of a wide range of cementing media, he was unable to subdue with consistent regularity the tendency of the polished slice to peel away from the glass mounting slide. We await better instruction on this important accomplishment.

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[2] Now Mico Instrument Company.

[3] Now Chief Geol., International Nickel Co., Ltd., Ontario.

[4] Now Ass't Prof. of Mineralogy and Mineragraphy, Calif. Inst. Tech.

[5] Research Assoc. in Geol., Harvard.

[6] Preparator, this Laboratory.

### *Abrasives*

It need only be mentioned at this time that the use of metal laps for final polishing requires abrasives far finer and more accurately sized than will suffice for polishing on fabric laps. Special means must therefore be employed to secure the suitable powders. The procedure outlined by Vanderwilt (1928) is substantially the same as now followed. The metal laps are vastly more economical of abrasive than is the older method; therefore, all the surroundings are cleaner and danger of injuring the specimen through accidental contamination by coarser particles is minimized.

Since the fundamental principle of our polishing method is gentlest possible treatment of the specimen from the very beginning, the preliminary flat surface cannot be secured, as previously, by grinding down a lump of the ore against a coarse wheel. Instead, the specimen is obtained by cutting a slice from the hand specimen by a special diamond saw, procured from the Mico Instrument Co.; this yields an almost ground-glass-smooth surface which is entirely acceptable for the succeeding stages of fine-grinding and polishing. For the examination of some given portion lying near the center of a large specimen, the part in question is removed by a special diamond bit, having a thin wall; it is rotated against the specimen by being clamped in an ordinary drill press; from the short section of resulting core a slice is sawn for mounting.

### *Mounting*

Polishing by machine virtually requires that the specimens be of uniform shape and size. For use with the first machine we secured from the American Brass Company a specially drawn rectangular brass tubing $1\text{-}\frac{1}{2}\times 1\text{-}\frac{1}{8}''$ O.D., from which were cut sections $\frac{7}{8}''$ long. The specimen was cemented in one of these boxes by means of a special sealing wax, and backed with plaster of Paris. After several thousand specimens had been so mounted, we found that every kind of wax we tried eventually warped or shrank or otherwise became useless.

In the search for a substitute, molded bakelite suggested itself; and after a trial specimen mounted in bakelite and polished was found at the end of three years to be in as satisfactory condition as at the beginning, we abandoned the mounting in brass tubes in 1927, disposing of our large unused supply of tubes to those who had adopted that scheme. Since that time, all our specimens have been mounted in rectangular blocks of molded bakelite of the same dimensions as before. See Fig. 2. The underside is recessed centrally to prevent rocking on the microscope stage.

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[7] Now Geologist, Cerro de Pasco Copper Corpn., Peru.

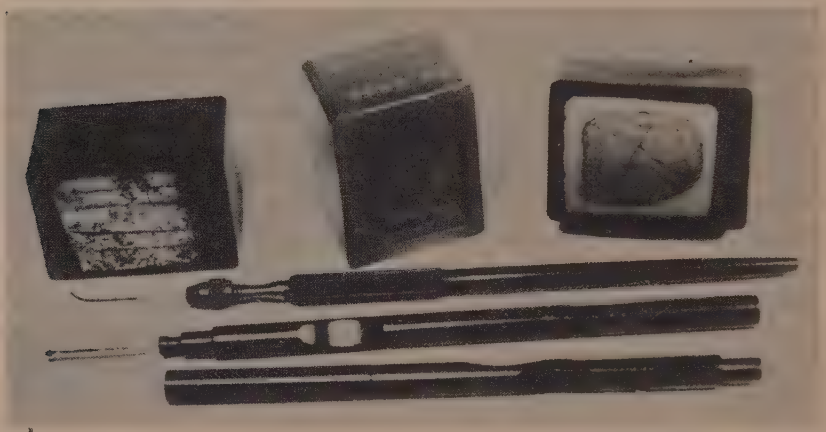

FIG. 2. A. The bakelite mounts, method of numbering, and, at right, use of Wood's metal inset for mounting heat-sensitive specimen.

B. Standard scratching needle in holder.

C. Platinum loop; holder in open position.

D. Platinum loop; holder in closed position.

Note reflection of platinum wire and of needle, also of their shadows, in mirror surface of left-hand specimen.

This method of mounting, suitable not only for solid specimens but also for single crystals, grains, powders and concentrates as fine as 400 mesh, has now been rather widely adopted. We strongly favor mounts of rectangular section instead of the circular section which some have been led to adopt on account of lower initial cost of the molding die. Besides the fact that, when accidentally dropped, the rectangular mount will not roll away, collar-button fashion, there are the great advantages that the area of surface is greater, that the numbering can be easily impressed on the side of the mount where it is in view during study, and also that any given feature on the specimen can be precisely and instantly located by the mechanical stage or other simple coordinate system.

By an appropriate holder on the stage it is possible to remove a specimen for washing or for some special test, then return it so that the exact spot initially centered is restored automatically to that same position. Since all our microscopes, including the microphotographic equipment, are calibrated to the same coordinates, it follows that any given feature, such as a certain tiny grain, can be recorded as to coordinates and specimen number, and then can be instantly found by any other worker at any later time on his own instrument. This is an enormous saver of time, above all in microphotography at high powers.

Each specimen mount is clearly and permanently numbered on one end by impressing the district symbol and the appropriate number (e.g., BIS 1361-H; BVD 14869—Bisbee and Bushveld, respectively) into the bakelite by means of a hardened steel numbering machine set in a small press. The number is impressed twice on each specimen so that by no chance shall there be obliteration. The old scheme of painting the numbers on was ever an abomination.

Prior to mounting, the specimen is given impregnation by bakelite resinoid baked for 4 hours at 90°C.; this is especially necessary for porous or friable materials.

With a pressure of about 5000 lbs. per square inch we mount our specimens at a molding temperature of about 125°C. With a very few exceptions, involving some pyrrhotite ores and certain specimens containing the richest silver minerals, we have detected no sign of decomposition or modification by the mounting operation, such as described by Bateman (1929). We have tried a considerable number of other plastics, certain of which mold at somewhat lower temperatures than bakelite, also a variety of cements that do not require any heat; but thus far we have found nothing so generally satisfactory as bakelite. When dealing with specimens which we think the molding temperature might affect, we "solder" the specimen in a *hollow* bakelite mount (which we mold specially for that purpose) by running in molten Wood's metal (M.P. 70°C.) under pressure, then letting it set. This works satisfactorily.

Our bakelite-mounted specimens now number over 6000, including a considerable number remounted from the old brass tubes. An occasional molding (4 at a time) goes wrong; but the great majority, including specimens over 9 years old, are entirely stable and in every way satisfactory.

## MICROSAMPLING

The experience of this Laboratory has led with increasing emphasis to the conclusion that determinative procedure must be suited to dealing with the smallest possible grains. A great expanse of homogeneous material more often than not involves little obstacle to identification. There is room to allow all the necessary tests to be readily applied, and repeated when necessary; interference by other minerals as to chemistry and color is minimized; all conditions are at their best. But determinative difficulties multiply as the grains grow smaller. Moreover, naturally enough, the less common minerals and the rarer elements are most likely to occur in tiny grains. It is these in particular that need identification, not only for the mere satisfaction of completeness but also for the significant genetic clues that such constituents so commonly afford. All our technique has therefore been designed to go as far as possible, first in disclosing the tiny grains by the best attainable polishing, and then in mastering the identification of these tiny constituents.

For microchemical, spectrographic and $x$-ray determinations, it is essential to remove from the polished surface an uncontaminated sample of the mineral in question. For this purpose the microdrill described by Haycock (1931) was further perfected at the hands of G. A. Harcourt by improvement of bearings and guide so that it turns at high speed with beautiful steadiness, by an arrangement whereby it may at will be swung either to a position where the point of the drill is exactly in the optical axis of the microscope or to a position entirely out of the way, and in connection with a microscope having a mechanical stage that can be raised and lowered. Dr. Harcourt's description of the drill appears on page 517 of this Special Number.

The drilling can now be held within the limits of a grain having a surface exposure as little as 0.02 mm. in diameter. Thus may be secured a sample for spectrographic determination without any danger whatever of contamination of this sample from adjoining grains, unless the contamination is accomplished by drilling *through* the grain into another mineral that lies below the polished surface. In case the texture of the ore suggests that there may be danger of this latter outcome, or in case the amount safely obtainable from any single grain is insufficient, an adequate sample that is probably pure can be usually secured by drilling tiny amounts from a number of different grains of the same mineral, taking care to drill only very shallow depressions in any one grain; the aggregate of the drillings from the several grains constitutes an adequate sample.

Reference should here be made to the aids for quantitative estimation of the components of an ore in the form of special micrometer eyepiece grids reading directly in percentages which we had made in connection with the quantitative microscopical study by Dr. E. Thomson (1930).[8]

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[8] Now Assoc. Prof. of Mineralogy, Univ. of Toronto.

## MINERAL IDENTIFICATION

### *General Treatises*

The first study at Harvard of polished sections of ores was made in 1909–10 by the late C. T. Brodrick[9] and the writer. We found all too frequently grains of material that we were unable to identify either by our own efforts or from what was then available in the literature. This was evidently a universal difficulty at that time, so that it was either necessary to make a guess at mineral identification or to designate many species as "unknown."

Therefore, it was decided to undertake a systematic determination of the opaque minerals. The major execution of this task was undertaken in 1911 by Joseph Murdoch,[10] who brought to it a noteworthy devotion and resourcefulness. At the time Murdoch's book "Microscopical Investigation of the Opaque Minerals" (1916) went to press, the most important existing paper on opaque mineral identification gave partial tests for 37 varieties. Murdoch's treatise included systematized identification data for 186 definite varieties besides disposing of many other names that had been applied to materials which his study showed to be identical with better established varieties or else obvious mixtures. The new science was christened *mineralography*, since it bears the same kind of relation to the broader field of mineralogy that petrography bears to petrology and metallography to metallurgy. This was the first systematic and comprehensive work on opaque mineral identification. The diagnostic criteria, the arrangement of data and the general conception of the tabular presentation have set the style for nearly all of the several treatises that have since appeared.

One of Murdoch's important accomplishments had been the assembling of a suite of all the well-authenticated varieties of opaque minerals which he had been able to secure during five years of quest. This became known as the standard Murdoch Suite; with its progressive refinement, and its gradual enrichment chiefly from the great mineral collection administered by Palache, it has remained the indispensable basis of all our determinative work of the last twenty years.

The next important improvement of opaque mineral identification was started by C. M. Farnham,[11] who after several years in the mines had returned for graduate study. Farnham recognized some of the shortcomings of Murdoch's work and aimed to correct these and also to increase the number of diagnostic tests. With the Murdoch Suite as a basis, he was able to advance toward these objectives. As W. M. Davy at the Massachusetts Institute of Technology was then engaged in a similar study, these two wisely decided to pool their results, which in due time were published (Davy and Farnham—1920).

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[9] Later Chief Geol., Russio-Asiatic Corpn., Urals and Siberia.

[10] Now Ass't Prof. of Geol., Univ. of Calif. at Los Angeles.

[11] Now Consulting Geol., Barre Plains, Massachusetts.

E. E. Fairbanks,[12] after some study as a special student at the Massachusetts Institute of Technology, came to our Laboratory to work with the Murdoch Suite and familiarize himself with the technique then employed. Shortly afterward he brought out as editor (Fairbanks—1928) an interesting book on laboratory procedure to which chapters were contributed by various specialists, whose willingness to do this resulted from his own enthusiasm.

After several years as Instructor in this Laboratory, where he contributed to every phase of our mineralographic technique as then in use, M. N. Short[13] went to the U. S. Geological Survey, where he had unusual opportunity to assemble a second standard suite of minerals analogous to the Murdoch Suite. Interchange of specimens between the two suites, which were studied at both ends of the line, helped more than anything previously had done to discover errors of identification. Short became a recognized authority in this field, bringing out (1931) what we at Harvard regard as the most reliable of the treatises that have thus far appeared on identification of the opaque minerals. As Short had been recalled to Harvard as lecturer for 1927–28, when the technique of this Laboratory had been further advanced, it will suffice to refer to details in his treatise for several of the topics considered later. Dr. Short is now engaged in a thorough-going revision of his book.

Farnham (1931) published a revision of the earlier work by Davy and himself, incorporating a number of improvements and corrections. This later work, though done elsewhere, is looked on at Harvard with the interest that comes from early association.

### *Physical Properties*

*Hardness.* While the old method of polish by cloth laps was in use, much could be determined as to relative hardness of the minerals by observing their relief against some known species present in the section, such as quartz, pyrite or sphalerite. But since the relief was a consequence both of the actual hardness-difference between adjacent minerals and of the method and duration of polishing that had been applied to the particular specimen, hardness distinctions made in this way were only very roughly quantitative. With the perfecting of polish so that now the surface is almost optically flat regardless of the varying hardnesses of the minerals involved, that former rough and ready test of relative hardness is practically eliminated.

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[12] Now Representative, Science Service, New York City.

[13] Now Prof. of Petrography, Univ. of Ariz.

We employ two methods for ascertaining hardness. The approximate method uses a bent needle mounted in a holder of standard length and weight so that the observer becomes accustomed to a standard leverage as he attempts to scratch the polished surface and thus to a standard range of pressures which he applies. Sharps' No. 8 needles are used; and whenever a needle shows under the microscope the first signs of wear it is discarded for a new one. About three millimeters from the point, the tip portion is bent about 50° out of line. This bending is easily accomplished in a wholesale way by gripping the very tips of an entire packet (25) of needles in a heavy steel vise which prevents the temper being drawn from the points when a narrow, intense blow-pipe flame is directed along the row of needles just above the vise until they redden and can be simultaneously bent over to the proper angle. This bending of the point enables the needle to be brought readily between the specimen and the objective and yet allows the actual scratching point to be drawn across the mineral at the fairly steep optimum angle for producing a scratch with least pressure. The standard holder adopted is a broach holder such as used by dentists. These can be purchased at insignificant cost from S. H. Reynolds Sons Company, Boston. The hard-rubber handle is ribbed to prevent turning while held gently in the fingers, and the neat little steel compression chuck grips the needle firmly, yet allows instantaneous replacement. See Fig. 2.

The precision method of determining hardness is accomplished by an instrument built for the writer in 1914 in the shops of the Geophysical Laboratory in Washington. When first used, a sharp needle was employed as the scratching point. S. B. Talmage[14] later experimented with the instrument and after various substitutes for steel had been tried, including agate and sapphire, we finally decided to standardize on the diamond. Dr. Talmage (1925-B) described the instrument and published a table of hardnesses as measured by its means. Since that time, with the cooperation of Dr. E. B. Dane, Jr., the precision of the instrument has been materially increased in a variety of ways, including the substitution of sapphire cone bearings for the previous hardened steel cups; the mechanical suspension of the balance beam and the micrometer adjustment for balancing it at zero are now essentially perfect. The precision of the instrument therefore depends upon the constancy of the diamond point, that is, upon its retention of sharpness and on its duplicability if replacement is necessary. Our diamond point (or blade, really) was made by Arthur A. Crafts & Co., of Boston. After several years of use no blunting by actual wear has been detected. Before certain guards were introduced, however, an occasional accident caused a chipping of the sharp edge; this was immediately disclosed on the first ensuing trial with the instrument, whereupon the diamond point was sent back to the makers for resharpening. When they first made the point, they took a highly enlarged photographic profile of its edge; when resharpening is necessary, they merely duplicate this profile. Each time the point has been resharpened it has exactly duplicated the readings it previously gave. Some years ago while our equipment was being moved to present quarters, the diamond point was so badly damaged that it had to be discarded and a new one made. We were fearful lest the entirely new piece of diamond used might have actually different hardness characteristics from the one we had first employed, since, although the mineralogist looks upon the diamond as of constant hardness, the diamond driller knows that different diamonds vary greatly in resistance to wear as well as in brittleness. When the new point was tried out on a considerable number of the minerals whose hardness had been established by the old point, we found the hardness readings the same as before.

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[14] Now Prof. of Geol., New Mexico School of Mines.

It therefore appears that here is an instrument which is duplicable within the necessary limits of accuracy. So far as we are aware nothing of corresponding precision is in use elsewhere, except in Mass. Institute of Technology. This seems unfortunate, since hardness is an essential and dependable characteristic of a mineral and this instrument will test hardness with beautiful precision; moreover, it would be regrettable to have differing arbitrary data on hardness arise from the use of instruments that have not been designed to give standardized results. Advantages possessed by this instrument over the microcharacter of Bierbaum (1923) were listed by Talmage (1925 B, pages 541–42). Further experience adds the following advantages: (1) The dulling of the diamond point is detected more readily and, therefore, earlier; (2) dependable tests can be made on much smaller grains, and there is no danger of the scratch reading through to an unconcealed different mineral that lies below; (3) recognition of the thin, clean "standard" scratch is more sensitive and reliable than the actual measurement of width of a deeper scratch—this is especially true on brittle minerals, N.B. the microcharacter was designed to test soft-bearing metals which tend to give smooth, ductile scratches whereas the ragged and variable scratches likely to be produced on minerals are pictured by Hodge and McKay (1934) together with the highly variable measurements of width that inevitably result.

Inasmuch as the hardness is determined by the production of a faint but definite "standard scratch" on the surface of the mineral, it is essential that the area to be tested be entirely smooth with respect not only to absence of other scratches but also freedom from pits and undulations. The relief-free mirror polish on even the hardest minerals by the lead-lap method affords an ideal surface for the determination of hardness by this instrument. Its precision and control are such that four parallel but perfectly distinct scratches can be made, at successively different settings of the balance weight, on a mineral grain not more than one fiftieth of a millimeter in diameter. As four successive tries ordinarily suffice to arrive at a scratch of the intensity defined as "standard," it follows that the hardness of grains even down to this minute size can ordinarily be ascertained reliably. By drawing a scratch across adjacent minerals their relative hardness is beautifully disclosed even though no relief whatever from the polishing is to be seen at their boundary.

*Cleavage.* D. H. McLaughlin[15] (1917) noted that certain relatively soft minerals, such as bornite, which do not ordinarily exhibit cleavage either in the hand specimen or in polished section, can be made to disclose this property, in a way analogous to production of the "percussion figure" of mica, by pressing the point of the scratching needle vigorously into the polished surface. Orientation of grains may thus be determined even if the mineral is optically isotropic.

*Specific Gravity.* G. V. Douglas,[16] A. W. Waldo,[17] H. Berman[18] and G. A. Harcourt[19] have in turn sought to develop a reliable method for determining specific gravity of a minute particle of a given uncontaminated mineral grain removed from the polished surface. None of their ingenious schemes, however, has yet overcome the difficulty occasioned by surface tension of the immersion liquid, which becomes aggravated in inverse proportion to the weight of the particle to be tested. Since each tested grain weighs a small fraction of a milligram, the disturbing effect of surface tension has thus far prevented the attainment of reliable results. The subject deserves further effort.

*Magnetism.* This useful determinative test encounters serious limitation when applied to polished sections in which the magnetic grains are small and scattered. A first trial involved bringing a magnetized needle in the field of the microscope in a balanced position and passing it closely above the polished surface. If one end of the needle came near enough to a magnetic grain, the needle would be drawn or repelled and balance upset. But this was an extremely precarious scheme. H. E. McKinstry[20] devised a very satisfactory substitute. After a needle has been magnetized it is cut in two right through the eye. The smaller part, a tiny curved piece of steel, is neatly cemented at its middle to the end of a 3-inch length of horsehair, and by fixing the opposite end of the horsehair appropriately, one has in effect a miniature "horseshoe magnet" supported by a "spring" just above the surface of the polished section and in the axis of the microscope. By then drawing the specimen systematically under the magnet by means of a mechanical motion of the stage, each grain suspected of being magnetic can be tested; if the grain proves to be magnetic, the observer at the microscope sees the little magnet drop sharply against the grain and hold there.

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[15] Prof. of Mining Geol., Harvard.

[16] Now Prof. of Geol., Dalhousie Univ.

[17] Now Research Asst. in Mineralogy, Penn. State Coll.

[18] Research Assoc. in Mineralogy, Harvard.

[19] Instructor in Mining Geol., Harvard.

W. D. de Laguna[21] has recently essayed some tests whereby minerals of lower magnetic permeability then magnetite and pyrrhotite might be made to disclose the magnetic property by examining them when in the influence of a strong magnetic field. Not enough progress has yet been made with such tests to insure their success, but in any case their promise has not yet been killed off. Some of the newer alloys of extremely high magnetic permeability can be had in the form of relatively fine powder and when such powder is dusted over the inclined surface of a polished section, particles of it tend to adhere to such grains in the specimen as are magnetic. There is still possibility of developing something useful in this direction, but thus far practical difficulties have been encountered through insufficient fineness of the magnetized powder and too brief retention of its full magnetic power so that fresh supplies must frequently be secured.

*Electrical Conductivity.* C. M. Farnham sought to measure the electrical conductivity of sulphides by bringing into contact with a given grain on the polished surface two needle electrodes in a circuit that included a voltmeter. Promising results were secured. Three lists of minerals, those which were virtually perfect conductors, those which were approximate non-conductors and those which stood in an intermediate position, were included by Farnham in a report submitted in connection with his studies for the Master's degree. This method was carried further and the lists extended in the book by Davy & Farnham (1920). Later workers in our Laboratory, however, found great difficulty in securing consistent measurements on minerals of the intermediate list.

The late R. D. Harvey[22] in time undertook to apply the conductivity test under rigid control. Dr. Harvey's paper (1928) records the variety of efforts that he made toward standardization and the results he secured. His apparatus involves terminals of standard size and shape applied to the specimen at a standard distance apart and at a standard pressure; for it was found that if any of these factors were varied, unreliable results were inescapable. The use of his apparatus and methods gives the best results that we have been able to secure; but the chance of erratic readings is still so high that we have virtually abandoned this approach toward mineral identification.

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[20] Now Consulting Geologist, New York City.

[21] Graduate student, Harvard.

[22] Later, Petrographer, Cerro de Pasco Copper Corpn., Peru.

*X-Ray Analysis.* Through cooperative arrangements, first with the Department of Metallurgy and later with the Department of Mineralogy, it has been possible to study the atomic structure of the opaque minerals by means of *x*-ray diffraction photographs. A. W. Waldo (1935) was the first in our Laboratory to attack this subject systematically. He studied the copper-bearing minerals and in his publication of the resulting data he has performed a distinct service in devising a scheme of indexing whereby the diffraction lines furnished by any material can instantly be compared with those known minerals which give closely similar patterns; thus identification is greatly facilitated.

Application of the *x*-ray method to the whole range of ore minerals is now being carried forward by G. A. Harcourt with improved tubes and casettes, and under conditions that lead tc more than mere determination of spacing of the atomic planes and empirical diffraction patterns. He has so perfected the technique that satisfactory powder photographs can be secured from as little as 0.02 mg. of material. By means of the microdrill, pure material in adequate amount for identification can thus be secured of a mineral even if a member of an extremely fine intergrowth. The details of this work are described by Dr. Harcourt in this Special Number.

### *Optical Methods*

*Color.* On a well polished specimen, color is the first quality of the mineral that impresses the observer at the microscope. Many of the colors are so distinctive as to afford instant identification of the mineral, but since the vast majority of the opaque minerals fall in the "grays" and "whites," the color differences are too small to be identified by reliance on one's color memory. Moreover, the "color interference" caused by adjacent grains of different color is surprisingly serious. Therefore, if color is to be used as a diagnostic property for more than a relatively small number of the more intensely colored minerals, some rigorous scheme of color measurement or color comparison is necessary.

Murdoch met this situation by so shaping his specimens that there could be brought in juxtaposition under the field of the microscope the mineral whose color was to be determined and a known mineral of approximately similar color used as the standard of comparison. By this means, combined with his unusually accurate color sense, Murdoch was able, I am convinced, to make useful color distinctions which succeeding workers have failed to duplicate, partly because they have been unwilling to spend the patient care he used. For a time, therefore, color as a diagnostic character fell into disuse and even disrepute; this is certainly regrettable.

With the cooperation of A. W. Pinger[23] in 1921, color was again attacked by the comparison method, using two microscopes connected by a comparison eyepiece instead of the more laborious and less satisfactory method used by Murdoch. S. B. Talmage (1925-A) inherited this equipment and carried forward a range of experiments which finally resulted in the production for us by the Eastman Kodak Co. of three colored wedges and a neutral wedge, similar to those used in their standard optical colorimeter. The principle is that by appropriate position of the three standard color wedges in the beam that enters the vertical illuminator it is possible to induce upon a standard (colorless) reflector a synthetic color which exactly matches the hue of the color reflected by the mineral being tested, and by appropriate placing of the neutral wedge the intensity of this synthetic hue is likewise matched with the unknown mineral. By recording the position (in distance from the thin or zero end) of each of the four wedges as they stand when this match is secured, one attains a four-number quantitative specification of the color of the mineral tested. The scheme is correct in principle but has drawbacks in practice, partly because the considerable thickness of glass interposed in the form of wedges "muddies" the color, and partly because, with four independent variables, a good deal of fitting and trying has to be done before perfect match is secured; the task is,therefore, extravagant of time. For the present we have returned to the comparison of the unknown against a succession of known specimens until approximate match is attained.

Dr. Dane and the writer are now engaged in the design of a new color comparator which we hope will incorporate the advantages of the wedge colorimeter method without its disadvantages. If these hopes shall be realized, it should be possible to use color as one of the most simple and reliable steps in mineral identification.

*Internal Reflection.* The color of a mineral, as shown by such light as happens to be reflected through it from fractures and from the boundaries of other minerals, deserves better use than that which can be made by light that happens to fall obliquely on the specimen. The annular lamp known as the Silverman Illuminator was, therefore, adopted by us in 1924 and so arranged that by the throwing of a switch the specimen could be examined at will by vertically incident light or by the oblique beam from the Silverman Illuminator; this gave, respectively, the color reflected from the surface and the color, if any, reflected from within the grain. It was later found that the internal reflection shows up as well or better when an intense beam of light is passed through a nicol prism and thence to the specimen by a vertical illuminator. Best of all is the type of oblique illuminator and attendant special objectives marketed by Leitz under the term "Ultropaque" and by Zeiss and others under the name "Epi-Condenser Illuminator." By this means internal reflection even of grains so tiny as to require oil immersion objectives can be studied satisfactorily. Our microphotographic equipment includes the ultropaque scheme of illumination.

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[23] Now Chief Geologist, New Jersey Zinc Co., Franklin Furnace.

*Reflectivity.* Attempts by the writer in 1927 to measure the intensity of reflection from the polished surfaces by means of a cuprous-oxide cell were quite without success. By 1934 photoelectric equipment had been so greatly improved and reflectivity measurements by others seemed so promising that it appeared advisable to renew our efforts, especially as the quality of polish then available to us was not only far better but also much more uniform than before. J. H. Moses undertook this task. He assembled a combination of equipment somewhat different from that used by preceding workers, the central item being a high-sensitivity "Photox" cell made by Westinghouse. He worked with the Murdoch Suite, which by that time had been rigidly checked spectrographically by Dr. Harcourt. Since the investigation was primarily for the purpose of simplifying and confirming mineral identification *in polished section,* in which the crystal orientation is usually not known, Moses concluded that it was useless to employ plane polarized light. Moreover, his experimental work showed that although reflectivity does vary with orientation, in only a relatively small proportion of the total number of opaque varieties does orientation affect the reflectivity by more than 1%, which was the net limit of error accepted by Moses as about the best that can be attained under present conditions. He found that different specimens of the same mineral, when equally well polished and when shown spectrographically to be similar, will ordinarily give reflectivity measurements that check to within about 1%; but if the composition is variable, either because of isomorphism or through sub-microscopically disperse "impurities," greater variations are to be expected. He showed, too, as we had suspected, that quality of polish has a pronounced effect on reflectivity; for example, on various samples of pure copper well polished, readings checked at 32.4 (arbitrary galvanometer units); but the same copper with a polish described by our standards as "fair" gave a reading of 31.1; and a "poor" polish, 29.8. It is partly on this account that the results secured by Moses show numerous disagreements with data of other investigators whose method of polish, even though high "burnish" is secured, does not give the optically plane surface like that yielded by metal laps.

Moses (1936) tabulated the opaque minerals in order of their reflectivity. Over a total range of 50 galvanometer units (which could be read usually to tenths), he found that the minerals are pretty well scattered; also that most minerals which come close together in his reflectivity table can be readily distinguished by some simple test or combination of tests, such as hardness, polarization, or etch behavior. Dr. Moses expects soon to publish the description of his equipment and methods and his reflectivity data for the Murdoch Suite.

The color comparator now being designed will, in reality, achieve its object by measuring the reflectivity of the minerals for each of several wave lengths.

It may be concluded that reflectivity is a useful help in mineral identification, but in its present state of application it is neither fool-proof nor all-sufficient. The precautions that have constantly to be observed against disturbing influences indicate that it is not a method to be used by a relative novice like a penny-in-the-slot machine. It is also clearly indicated that if various investigators are to reach approximate agreement on reflectivity data, there must be better standardization on polish than now exists.

*Polarization.* The interesting phenomena disclosed by opaque minerals in polarized light were long used by us only in an empirical way; that is to say, with one nicol color changes were recognized for a few minerals, and with crossed nicols four classes were established, namely, those in which polarization effects can not be detected and those which show respectively feeble, moderate and strong anisotropism. The desirability became evident of confirming and clarifying the conclusions regarding these phenomena that had been published by others and of proceeding as far as might be possible toward duplicating for the opaque minerals the marvelous results achieved by applications of polarized light in thin-section mineralogy.

E. A. Goranson,[24] well trained in physics and in mathematics, undertook this study. As his interesting and important results (1933) are soon to be printed, only the briefest reference to the most vital conclusions will here be made. From a welter of scattered and more or less abstruse and theoretical writings, Goranson has assembled a straightforward and useful formulation of the relations between refractive index, absorption index and reflecting power, of the role of each in opaque-mineral optics, and of the deductions as affecting instrumental procedure and the phenomena of surface color and reflected dichroism. The distinction is explained between true interference colors due to phase difference in thin sections and the polarization colors due to difference in amplitude for reflecting minerals, and the great limitations thereby imposed when dealing with the latter are listed and clarified.

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[24] Now Geologist, East Malartic Mines, Ltd., P.Q.

The phenomena that can be utilized for the reflecting minerals and the optimum conditions for observing them are set forth. The very practical conclusions are drawn that deviations from optically plane polish introduce erratic and disturbing anomalies, that all adjustments of the microscope and the illumination must be made with extreme precision, that anisotropic effects are most pronounced and therefore for feebly anisotropic species are most readily detected when the analyzer is slightly (i.e., 1°–5°) off the 90° position with respect to the polarizer, and that accessories useful in transmitted light, such as gypsum plate, etc., have little or practically no influence on anisotropic effects in reflected light.

## *Chemical Properties*

*Etch Tests.* Mineralography inherited from metallography the scheme of etching with various reagents, primarily for the purpose of establishing identification, secondarily for the purpose of revealing structure. It had been and still is the common practice in metallography to etch the entire surface of the specimen, since the ordinary metallurgical specimen is uniform throughout. This procedure was followed in our early work with ores; but we found it had two drawbacks; first, the normal behavior of a given mineral to a given reagent might be interfered with when the reagent was in contact also with one or more additional minerals; second, after each etching it was necessary to repolish the entire surface; this was extravagant of time. We discovered that quite satisfactory results could be secured by etching a tiny area of a given grain while in processes of observation under the microscope, and that practice has now become general. The reagent was first applied by a micro-pipette made by drawing a glass tube to a fine capillary. But difficulty was commonly experienced in getting the reagent to "feed" in right amount onto the specimen, and also the specimen was often scratched by the sharp edge of the pipette. We finally came to a scheme which has now become our standard—that of a platinum wire loop mounted in an appropriate handle. See Fig. 2. The handles that we use are turned from hard rubber and are rather similar to, but smaller than, a fountain pen; like the pen point, the platinum loop is protected when not in use by a removable cover which, when in use, is slipped on the opposite end of the holder to give it extra length. The wire is readily cleaned and, therefore, can be used for one reagent after another without any danger of contamination. The loop picks up invariably almost the same identical quantity of reagent; the area of the etch reaction is, therefore, practically constant. The little lens-like drop of reagent held in the loop constitutes, as a matter of fact, a powerful magnifying lens. The result is that when the loop with its reagent is brought into the field of view of the microscope and is in the act of being lowered to contact with the polished surface, this little liquid lens serves as an auxiliary to the microscope system and just before the polished surface is touched the area immediately underneath the drop springs into focus more highly magnified than before, so that the exact spot where the reagent is to be applied is seen with special clarity.

For many of the minerals, the simple etch reactions with one or more of the reagents now generally accepted as standard are highly useful for purposes of identification, but they are becoming supplemented more and more by microchemical reactions in the narrower and more precise sense.

*Microchemical Reactions*. Although the writer was one of the early students of Chamot, American leader in microchemistry, Harvard was late in applying these methods to identification ot the opaque minerals. After some pioneering efforts by K. K. Landes[25] and R. W. Goranson,[26] two men worked in our Laboratory who received instruction in this phase of the subject from Lindgren, and they, H. E. McKinstry (1927) and M. N. Short (1931), have helped to carry it to its present highly useful state. We have come to put increasing dependence on the methods and data assembled by Short, whose kindness in supplying us with advance editions of his tables has kept us in touch with the latest data.

*Spectrographic Analysis*. Through the enthusiasm of G. V. Douglas, a Hilger Quartz Spectrograph was purchased for our Laboratory in 1925, but before systematic efforts at its use for mineral identification had advanced very far he was enticed away to Rio Tinto. H. H. Chen (1927) established spectrographically the presence of molybdenum and vanadium in microscopically homogeneous galena from several Western mining districts where the oxidized ores are relatively enriched in those rare elements.

After a considerable amount of experience with the spectrograph in connection with geological problems at Queen's University, G. A. Harcourt came to this Laboratory and undertook first the systematic testing of the minerals of the Murdoch Suite and then the general problem of mineral identification by spectrographic methods. Approximate quantitative data are secured by various means, including rotating sectors of both the "wedge" and the "step" types. The sampling and testing processes have been so perfected that an uncontaminated component of an extremely fine-grained intimate intergrowth may now be removed, studied by *x*-ray and then, on the same sample, analyzed spectrographically. This exceedingly valuable technique is described by Dr. Harcourt in this Special Number.

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## MICROPHOTOGRAPHY

Ever-widening extension of mineralographic study whereby are encountered new and interesting relationships of texture, sequence and alteration, coupled with better polishing, could not fail to increase the desirability of good microphotographs. Growing recognition of the tremendous importance of the super-minute and improved technique for revealing it have imposed new burdens on the photography. The attempt to record important facts by sketches or camera lucida drawings is ordinarily to be discouraged because of likelihood of unintentional or subconscious distortion by either commission or omission.

Our own early experience in microphotography was gained chiefly at the hands of Murdoch who, in turn, was helped greatly by Prof. Albert Sauveur and Dr. H. M. Boylston, then of the Department of Metallurgy, from their rich background of metallographic technique. Procedure was standardized and various improvements incorporated through the skillful work of Short, Yates and Dane, each of whom has carried us successively farther toward satisfactory accomplishment.

After years of partly-satisfactory use of one of the well-known elaborate microphotographic units for opaque specimens and another for thin-section photography, and a growing realization of what seemed to us shortcomings in these as well as all the other models on the market, a new microcamera was projected. The design was improved in many ways through the mechanical ingenuity and sagacity in optics possessed by Dr. Dane. The instrument, built by Mann Instrument Company of Cambridge, was finished at the end of 1933 and has realized most of the high hopes that led to its inception. Although embodying many of the features of the better instruments now available, it differs in numerous important respects. Inasmuch as a complete description will soon appear (Graton and Dane, 1937), only the more outstanding features need here be listed.

The instrument accommodates either transparent or opaque specimens. It is, moreover, so designed that both those kinds of components in an appropriately prepared section may be simultaneously illuminated, each in its special way, studied and photographed; so that the varied relations of both ore and gangue minerals to one another and to each other can be recorded in a single photograph. Ahrens prisms of unusually large cross section afford polarized light for both transmitted and reflected work.

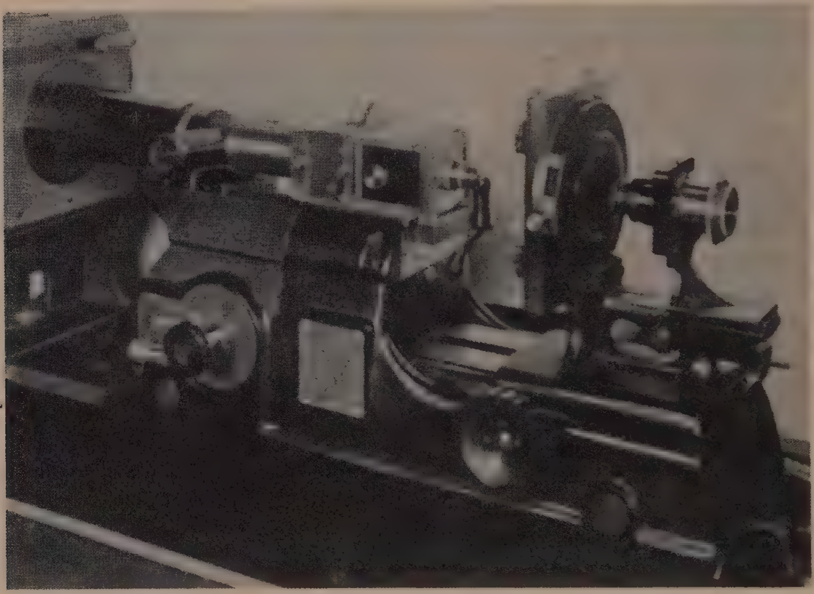

Fig. 3. Microscope Portion of New Precision Microcamera.

Perhaps the greatest departure from conventional design is in the fine-focussing mechanism, where back-lash is eliminated and the focussing attained by a motion of such precision that one division on the focussing scale equals 0.00001 mm., or about 1/54 of the wave-length of the mercury line by means of which this interval and the accuracy of the entire focussing mechanism have been checked by the interferometer. With so slow a fine-focussing motion, hand-focussing becomes extravagant of time and therefore is replaced by motor-driven focussing. These refinements in focussing are justified for the highest powers by the essentially optically plane polish now available, and are believed to put the precise control of focussing on a level not previously attained. It is found that when best possible focus is obtained, visibly evident impairment of that focus is produced when the focussing is changed by 3 to 10 scale-divisions (i.e., 0.00003–0.0001 mm. or 300–1000Å). Since no such exacting control over the focussing mechanism has heretofore been possible, it seems inescapable that much photography has been done at something less than the best focus that might have been secured from the optics employed.

Massive construction and best precision-instrument design help to afford accuracy, constancy, absence of vibration, etc. With our highest-powered combination of objective and ocular and maximum bellows draw, direct magnifications of well over 40,000 diameters can be secured. Such fantastic figures are, of course, in that range known as "empty magnification" and represent merely enlargement rather than improved resolution. But the instrument has a useful range up to 4–6000 diameters. Fig. 3 gives an idea of the microscope portion of the instrument.

## CONCLUSION

When writing the preface to Murdoch's book 22 years ago, I gave particular emphasis to the inexpensive equipment and the simple technique required for mineralographic investigation. Everyone who has followed the subsequent evolution of microscopy as applied to the study of ores will realize how fallacious that emphasis has proved to be. At long last, geology is becoming in respectable degree a quantitative science; this means a science attacked by instruments, and instruments of ever-increasing precision and scope. This is plainly true in crystallography and in petrography, as it is also in mineral synthesis and in geophysics. It is no less true in mineralography. Indeed, it seems fair to go far toward the conclusion that, just as in physics, chemistry and biology, those branches of geological science that are becoming most *instrumental* are the branches that are advancing most rapidly and soundly.

The task of correct and complete identification of the opaque minerals has proved surprisingly difficult. No longer can accurate results or even results sufficiently accurate for most practical purposes be gained by the simple means of so-called determinative mineralogy; nor by those rough-and-ready steps of polishing and testing which constituted mineralographic technique a quarter-century ago—they are as inadequate and outmoded as an automobile of corresponding vintage. New means of approach, new instrumental appliances, each usually more intricate and exacting than before, have had to be sought, devised and put to use. This trend will undoubtedly continue.

Unfortunately, and contrary to the hope I long held, most of those methods of quantitative precision, refined especially in recent years, which have contributed so splendidly to improved mineralogy of the transparent varieties have not yet been found of anything like corresponding usefulness when applied to the opaque minerals. For although it is now established that all the "opaque" minerals have some degree of transparency, the magnitude and perhaps even to some extent the nature of this transparency cannot yet be effectively put into harness, as it were, and made to pull out for direct diagnostic use such highly significant and beautifully quantitative data as indices of refraction, birefringence, extinction angle, optical character, optic angle, etc., which now constitute the modern stock-in-trade of the worker with transparent varieties. For the opaque minerals, only a few qualitative or semiquantitative equivalents have thus far been developed. Toward the filling of these great present gaps, effort in the future must plainly be directed, both through more resourceful instrumental assault and through ever deeper probing into the nature and significance of the crystalline state.

In the meantime, the problem of opaque mineral identification seems to be finding increasingly effective solution through the application of *x*-ray and spectrographic methods, combined with those techniques which insure uncontaminated samples of even the tiniest particles or the most intimate intergrowths (since this obstacle of fine grain and intermixture is especially serious among the opaque species). By the conjunction of these methods in skilled hands it is now possible to secure pure material from a particle not more than 0.02 mm. in diameter. And upon so minute a quantity of material as 0.02–0.002 mg., which is an amount just barely visible to the unaided eye when viewed on a glazed paper in intense light, it is now possible to determine such fundamental facts as the kinds, the approximate proportions and the space arrangement of the component atoms. This is, indeed, a long step toward the ultimate. When *x*-ray, under the extremely exacting conditions imposed by the infinitesimal quantities of sample, can be made to go still further in disclosing full details of the space lattice, and when spectrographic analysis shall have become more precisely quantitative, the task of mineral identification will presumably have been brought to approximate perfection. With the number and enthusiasm of the workers now engaged in this field, it is altogether probable that such a level of attainment is not very far off. Even then, the other properties, such as color, specific gravity, polarization, etc., when mastered, together with those already under control, will still afford useful diagnostic short-cuts. Moreover, unmeasured opportunities lie ahead for further discovery of the interrelations between the physical, optical and chemical properties, and for thus resolving these now diverse data into a compact and all-inclusive philosophy of the nature of crystals and of matter in general.

Except in a narrow sense, identification of the opaque minerals, to which this paper is so fully devoted, is not an end in itself. Like the determination of the kinds of bacteria, it has a broader and deeper use. There must be recognized the same kind of dangers in turning loose a microscopical specialist (who is nothing more) upon the problem of finding ore in a region of complex geological controls that there would be in turning over the stemming of a serious epidemic to a narrow specialist in microscopical bacteriology. But the time has definitely passed when the mining geologist is safe in relying solely on what some used to single out for worship as "the broad field relations." And the former pastime of looking condescendingly on the microscopical investigation of ores as high-brow and supertheoretical is no longer good sport, but tends immediately to challenge either the progressiveness or the mental integrity of whoever might still be tempted to indulge in it. Medicine has demonstrated not only the value but the absolute necessity of combining clinical and laboratory investigations. The profession of ore hunting will prosper and grow in merit in proportion as it learns to do the same.

The accomplishments summarized in this paper have been contributed by those responsible for them as increments toward that rapidly growing and imposing accumulation by many investigators in all parts of the world. I am confident that I speak for all those who have had a hand in these efforts at Harvard, including my colleague, Prof. Russell Gibson, who has shared in the supervision of these efforts, as well as for those associates who have aided in advancing other aspects of the science of mineralography, in recording our exhilaration at participating in the exploration and development of a new, specialized field. In this we have ever felt the contagious enthusiasm of that true scientist and delightful gentleman to whom this Special Number is dedicated.

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# THE DISTINCTION BETWEEN ENARGITE AND FAMATINITE (LUZONITE)

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## INTRODUCTION

For the past three years the writer has been working on the problem of studying minute samples of ore minerals by a method combining the use of the quartz spectograph and the *x*-ray powder camera. The method is being developed as an adjunct to the optical study of ore minerals in polished sections; and it is particularly adapted to the study of minerals which occur habitually in fine intergrowths and whose identity and specific properties are in many cases uncertain. The procedure involves excavating minute samples from very small areas in a polished section by means of an improved micro-drill, and utilizing them for powder photographs and spectographic analyses. In this way valuable qualitative structural and chemical data are obtained for comparison with the usual characters observed in polished sections.

## THE MICRO-DRILL

The drill used in the present work was patterned after that described by Haycock (1931). This consists of a 1/50 H.P. electric motor connected by means of a flexible cable to a rigidly mounted spindle which holds the drill (Fig. 1). The drill point is simply a No. 7 Sharp needle mounted in a pin vise chuck and supported close to the drilling point by a bearing. The spindle and drill are mounted rigidly in a frame in an inclined position so that the point of the needle is in the center of the field of the microscope when a polished section is in focus. The inclination of the spindle and drill is governed by the focal length and outside diameter of the objective used, leaving sufficient clearance so that the section may be brought into focus when it is lowered out of contact with the drill. In this position, the section may be moved about freely for examination, without danger of scratching the surface. The section is moved by means of a mechanical stage in which the specimen is clamped. Drilling is accomplished by raising the stage of the microscope until the section makes contact with the needle point.

The pin vise chuck, even with a supporting bearing, allowed considerable play because the taper of the needle did not allow an accurate fit. To secure accurate rotation the needle is mounted in V supports and held in place by phosphor bronze springs (Fig. 2). Dispensing with the chuck, the needle is attached to the spindle by means of a crude but effective universal joint, consisting of a bar forked at each end. One end fits over a tiny bar placed in the eye of the needle; the other over a similar bar in the hollowed end of the spindle. With this arrangement the eccentricity of the needle point depends solely upon the shape of the needle. The needles are remarkably round and straight but their sharp tips are rarely precisely upon their axis of rotation. This is fortunate because it is this slight eccentricity of the needle point which makes an ordinary sewing needle a good mineral drill. A few needles in each package are so far from being centered that they are of value only for large grains but the majority fall in the useful range. In operation the eccentricity of the needle point must be small in comparison to the size of the grain being sampled. The best performance which can be secured with the present arrangement is such that an area 0.02 mm. in diameter is affected when the drill is brought into contact with the surface of a mineral. The average mineral grain to be sampled is large in comparison to this minimum, and to secure material sufficient for $x$-ray or spectographic work the grain and section must be moved about under the drill with the mechanical stage.

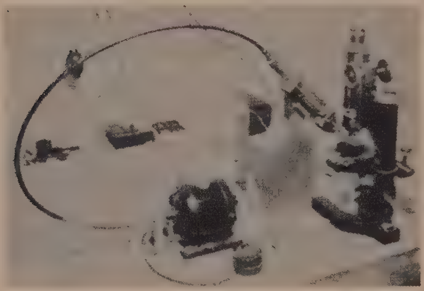
FIG. 1

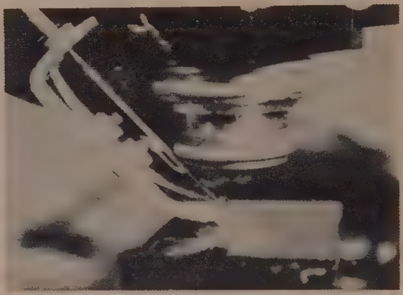
FIG. 2

### PREPARATION OF THE POWDER SAMPLES

The sample provided by the micro-drill accumulates at one side of the needle in a compact pile which may be transferred as a unit to a glass slide by means of a fine splinter of wood. A small drop of solution of collodion in ether is placed upon the sample, the particles of which immediately spread out in the drop and become evenly dispersed. When the drop has dried sufficiently to be handled and yet is still plastic, it is removed from the slide with the aid of a steel needle and rolled between the fingers into a tiny rod about 1/16 inch long. This is placed upon the glass slide again and a second larger drop of collodion-ether is attached to one end of it. When this is partially dry it is rolled again so as to form a non-diffracting holder for the specimen. When dry the mount is complete and ready to be placed in the camera. As many as 20 such mounts have been prepared in three hours and much of this time was consumed in examining sections and checking minerals and individual grains in order to select a particular grain for sampling.

Powder diffraction patterns are secured with a Debye type of camera of radius 57.5 mm. The sample is mounted in wax and centered by simply pushing sample and wax until the rod-like specimen lies in the axis of rotation of the specimen holder. This procedure is very simple and more satisfactory in all respects than a mechanical chuck. The mount is rotated by a telechron motor. The details of the powder method are fully described in the literature and will not be treated further. The advantages of the application of this method to the opaque minerals were pointed out by Kerr (1924).

## SPECTROGRAPHIC ANALYSIS

The spectrographic analyses are carried out with a medium Hilger quartz spectrograph. The logarithmic wedge sector, described by Twyman and Simeon (1929), has been adopted to provide analyses which are semi-quantitative. Excitation is accomplished by a direct current arc drawing 6 amperes from a 110 volt supply. Electrodes are of $\frac{1}{4}$ inch graphite shaped with a pencil sharpener and purified by baking in a stream of chlorine gas at 1000°C. The mineral sample is placed directly into a small cavity drilled in the conical tip of the lower electrode. The minimum size of sample that will give consistent results was studied; a compromise was found necessary between the conflicting objectives of a minimum sample and accurate quantitative measurements. A sample estimated to weigh between 0.002 and 0.0002 mg. was selected as a satisfactory standard.

Quantitative measurements depend upon the fact that the intensity of the spectrum of an element varies with the amount of the element in the sample. The effect of the logarithmic wedge sector, which rotates in front of the slit of the spectrograph, is to give wedge-shaped spectral lines of lengths proportional to the intensity of the radiation which caused them. The difference in the lengths of two lines is proportional to the ratio of their intensities; consequently, other things being equal, this measurement is proportional to the ratio of the amounts of the two elements present in the sample.

## ENARGITE, FAMATINITE AND LUZONITE

Enargite ($Cu_3AsS_4$) was described by Breithaupt (1820). Doelter (1926) lists thirty-six chemical analyses of enargite ranging from arsenic

19.47%, antimony none to arsenic 11.4%, antimony 6.4%. $X$-ray powder diffraction patterns of enargite have been studied by Kerr (1924), Frebold (1927), de Jong (1928) and Waldo (1935). A structure of the wurtzite type has been determined by Pauling and Weinbaum (1934). The rarer mineral famatinite ($Cu_3SbS_4$) was described by Stelzner (1873) from Sierra de Famatina, Argentine. Doelter (1924) lists analyses which range from arsenic 3.23%, antimony 10.9%, to arsenic 10.9%, antimony 21.78%. The mineral luzonite, which occurs only in indistinct crystals at the type locality, was described by Weisbach (1874). It is stated to have the same composition as enargite ($Cu_3AsS_4$).

Vom Rath (1878) considered famatinite to be isomorphous with enargite; from $x$-ray powder patterns de Jong (1928) concluded that the two minerals have the same structure, in which opinion he is supported by Schneiderhöhn and Ramdohr (1931) and Waldo (1935), and opposed by Frebold (1927), who obtained unlike powder patterns from famatinite and energite and concluded furthermore that luzonite is not a distinct species. Moses (1905) regarded luzonite as the same as enargite, on the basis of crystallographic measurements. Schneiderhöhn and Ramdohr (1931) came to the opposite conclusion from $x$-ray studies. Murdoch (1916), Farnham (1931) and Short (1931) regard luzonite as a variety of enargite on the basis of color difference and the existing crystallographic and chemical evidence. Klockmann (1891), on the other hand considered famatinite and luzonite as isomorphous, and unlike enargite.

Schneiderhöhn and Ramdohr recognize that luzonite has a crystal structure distinct from that of enargite and conclude that two solid solution series exist as follows:

Enargite structure
Enargite ———————— Famatinite
$Cu_3AsS_4$ $Cu_3SbS_4$

Luzonite structure
Luzonite ———————— Stibioluzonite
$Cu_3AsS_4$ $Cu_3SbS_4$

In the first series they do not believe that complete isomorphism exists; in the second series they consider that almost complete miscibility prevails.

It is believed that the confusion in the mineralogy of the enargite group is due primarily to the intimate intergrowth of minerals of the group. Competent investigators have obtained diverse results since chemical analyses, $x$-ray studies, and observations on polished sections could not be correlated.

Before presenting the results of such a correlation of methods it should be pointed out that if enargite and famatinite form an isomorphous series, only one representative of the series will occur in a given specimen if equilibrium is attained. If equilibrium is not reached during the formation of the mineral, zoning may result. Dimorphous forms are stable for different ranges of temperature, pressure and concentration, so that one form may replace another as conditions change from one stability range to another.

TABLE 1. SPECTROGRAPHIC DATA ON SPECIMENS OF MINERALS OF THE ENARGITE GROUP

| Diffraction pattern No. | | Locality | Color | Intensity measurements[1] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Fig. 3 | Fig. 4 | | | Cu | As | Sb | Ag | Sn | Fe | As-Sb |
| 1 | 1 | — | — | Silver | | | | | | |
| 2 | | Near Santiago, Chile | Grey | 11 | 7 | Tr. | — | — | 6 | 7 |
| 3 | 2 | Butte, Mon. | Grey | 11 | 10 | 5 | 7 | 2 | 7 | 5 |
| 4 | | San Pedro Mine, Argentine | Grey | 10 | 7 | 4 | 7 | 8 | 6 | 3 |
| 5 | | San Pedro Mine | Grey | — | — | — | — | — | — | — |
| 6 | | Butte, Mon. | Grey | 9 | 7 | — | 6 | — | 5 | 7+ |
| 7 | | Butte, Mon. | Grey | 11 | 6 | 3 | — | — | 9 | 3 |
| 8 | | Butte, Mon. | Grey | 10 | 6 | 1 | 6 | — | 6 | 5 |
| 9 | | Unknown | Grey | 10 | 6 | 1 | 4 | — | 3 | 5 |
| 10 | | Morococha, Peru | Grey | 12 | 8 | 5 | 7 | 4 | 3 | 3 |
| 11 | | San Pedro Mine, Argentine | Grey | 12 | 8 | Tr. | 8 | 2 | 9 | 8 |
| 12 | 3 | Tintic, Utah | Grey | 9 | 7 | 4 | 5 | — | — | 3 |
| 13 | | Ouray, Colo. | Grey | — | — | — | — | — | — | — |
| 14 | | Butte, Mon. | Grey | 8 | 4 | — | — | — | — | 4+ |
| — | | Cerro de Pasco, Peru | Grey | 10 | 5 | — | 8 | — | 5 | 5+ |
| — | | Unknown | Grey | 9 | 5 | Tr. | — | — | 1 | 5 |
| 15 | | San Pedro Mine, Argentine | Pink | 10 | 6 | 4 | — | 4 | 8 | 2 |
| 16 | 4 | San Pedro Mine | Pink | — | — | — | — | — | — | — |
| 17 | | Cerro de Pasco, Peru | Pink | 9 | 6 | 8 | 7 | 4 | 6 | −2 |
| 18 | | Cerro de Pasco, Peru | Pink | 12 | 7 | 10 | 9 | 9 | 9 | −3 |
| 19 | | Loope District, California | Pink | 10 | 6 | 6 | 8 | 4 | 2 | 0 |
| — | | Morococha, Peru | Pink | 8 | 5 | 5 | 7 | 5 | 6 | 0 |
| — | | Unknown | Pink | 8 | 1 | 5 | 6 | 2 | 4 | −4 |
| 20 | 5 | Tsumeb, South Africa | | Germanite | | | | | | |
| 21 | 6 | Butte, Mon. | | Colusite | | | | | | |
| 22 | 7 | Burra Burra, South Australia | | Sulvanite | | | | | | |
| 23 | 8 | Magma, Ariz. | | Bornite | | | | | | |

[1] The intensity measurements listed above are for the following lines: Cu 2824, As 2780, Sb 2878, Ag 3280, Sn 2839, Fe 3020 Å.

In polished sections of specimens of the enargite group two minerals commonly occur; one is grey in color, the other pink. They occur as a granular intergrowth showing neither zonal relationships nor evidence of replacement. Sections of material labelled enargite contain these two minerals and sections of material rich in antimony and identified as famatinite likewise contain both a grey and a pink mineral as a granular intergrowth. It has been noted that arsenic-rich ores contain only a minor amount of the pink mineral; antimony-rich ores contain a much larger proportion of the pink mineral. The two minerals respond identically to tests in polished section, having the same hardness, etch tests, anisotropism and constituent elements—if qualitative tests are relied upon. Luzonite differs from enargite only in its color, its characteristic lamellar twinning and lack of cleavage.

In figures 3 and 4 and table 1 are summarized the *x*-ray and spectrographic results of this investigation. In Figure 3 the enargite structure is represented by the powder diffraction patterns numbered 2 to 14. Patterns 15 to 19 represent the luzonite structure; 20 to 23 represent a few minerals which give patterns similar to the luzonite pattern. Pattern No. 1 is the diffraction pattern of silver; this pattern may be seen in some of the enargite films since silver was added to some of the samples for calibration purposes. In Table 1 the minerals are listed with the corresponding number of the powder patterns of figures 3 and 4, the color of the specimen, location and spectrographic analysis. The numbers under the elements are measurements in millimeters of the length of

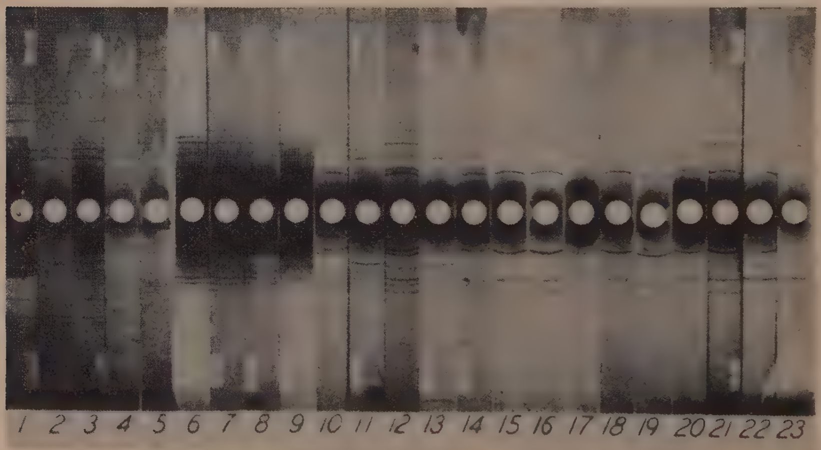

Fig. 3

selected lines due to Cu, As, Sb, Ag, Sn, and Fe. Each horizontal row contains values taken from a single spectrum and the values are comparable. Since one sample may have been slightly larger than another, or the exposure may have been slightly longer in photographing one spectrum than another, the values in different horizontal rows may not be compared directly. Due to the logarithmic wedge sector, each line increases in length by the same amount as the intensity of the spectrogram increases provided the proportion of the elements in the sample remains constant and conditions are standardized.[2]

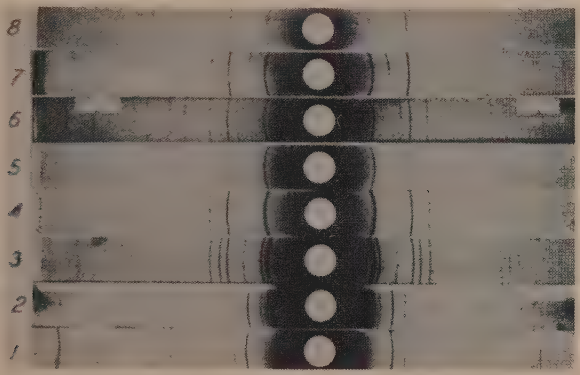

FIG. 4. Diffraction patterns were secured with copper radiation using a nickel filter.

As stated earlier, the difference in the lengths of two lines is proportional to the ratio of their intensities. The relative intensities in turn are dependent upon the relative proportions of the two elements concerned; consequently the figures in the last column of table 1 giving values of As minus Sb give a measurement which is independent of the variations due to the size of sample, exposure, etc., and is determined by the proportion of As and Sb present in the sample analyzed. Exactly what this proportionality is can be established only by preparing artificial mixtures of known composition which duplicate the substances being analyzed over the complete range, plotting the relative intensities secured from these standards against these known proportions, and finally referring the intensity ratios given by the minerals studied to the resulting calibration curve for evaluation. In the present case this has not been done; instead an attempt is made to draw certain conclusions directly from the As-Sb intensity values. A large value for As-Sb indicates high arsenic—low antimony; whereas a low value indicates low arsenic—high antimony.

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[2] This is true only when precautions are taken: 1, to select spectral lines not subject to erratic variations; 2, to select lines for comparison which lie close to one another in the spectrum; 3, to ensure constant excitation; 4, to ensure accurate alignment of the optical system; 5, to secure rapid rotation of the sector; 6, to ensure photography of a fair sample of the total radiation emitted by the mineral sample; 7, to ensure constant photographic technique.

Now if in this varied collection of minerals of the enargite group there is a fair sample of the range in the ratio of As to Sb which may occur in nature, then there should be a correspondingly representative range in As-Sb intensity values. These values range from 8 to $-4$ but it is a striking fact that all minerals having the enargite atomic structure range from 8 to 3 and the minerals having the luzonite atomic structure range from 2 to $-4$. In other words the enargite structures are arsenic-rich, the luzonite structures are antimony-rich; furthermore, the proportions of As to Sb do not overlap for the two groups.

These observations suggest very clearly that there exist two series; that the proportion of antimony in $Cu_3AsS_4$ may increase only up to a certain amount and still have the enargite crystal structure, and similarly that the proportion of arsenic in $Cu_3SbS_4$ may increase only up to a certain amount and still have the luzonite structure. The second series will be properly named the famatinite series, since ideal famatinite is the pure antimony compound.

$Cu_3AsS_4$————$Cu_3(As, Sb)S_4$ $Cu_3(Sb, As)S_4$————$Cu_3SbS_4$
Enargite Famatinite

While it is recognized that a mineral rich in arsenic having the luzonite structure and one rich in antimony having the enargite structure may eventually be found, the present statistics are much opposed to this possibility. In view of the rather widespread belief, based upon chemical analysis, that luzonite is an arsenic-rich mineral and that there is a mineral having the enargite structure but rich in antimony, one is reluctant to press the indications from the present semi-quantitative determinations; yet the suspicion is strong in the writer's mind that in the chemical analyses of these minerals that have been made too little attention has been given to the possibility of the occurrence of mixtures of two minerals, especially since the microscope reveals that intimate mixtures of enargite and luzonite are so common.

Whatever the final explanation may be, the conclusions to be drawn from the present observations are clear. It is therefore suggested that the relations may be as outlined above and that in the enargite series should be placed only minerals of this general group that have the enargite structure; according to the present study these minerals are all rich in arsenic. Similarly it may be that in the famatinite series belong minerals of the group having the structure of the mineral which up to the present time has been called luzonite; as is shown here these minerals are all rich in antimony. If this suggestion is correct, luzonite and famatinite refer to the same mineral series and are therefore synonymous. Since famatinite has date priority and refers to an antimony-rich mineral this name should be retained for the series.

In Figure 4 it will be seen that the diffraction patterns of famatinite (luzonite), germanite and colusite are closely similar not only in the number and position of lines but also in their intensities. Now the structure of germanite has been worked out by de Jong (1930), who found it to be of the sphalerite type with $a_0 = 5.290 \pm 0.005$ Å or possibly $10.58 \pm 0.01$ Å. Zachariasen (1933) has determined the structure of colusite by oscillation photographs to be of this same sphalerite type, with $a_0 = 5.304 \pm 0.001$ Å. It is thus evident that luzonite belongs to the same structure type. It has the sphalerite type of structure but since it is strongly anisotropic it is not of isometric symmetry.

Pauling and Weinbaum (1934) have pointed out that the structure of enargite is closely related to that of wurtzite, the hexagonal form of ZnS. The structural relations of enargite and famatinite are thus analogous to those of sphalerite and wurtzite.

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# ON SYNADELPHITE AND PLUMBOSYNADELPHITE

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## Identity of Synadelphite and Allodelphite

Synadelphite, essentially a hydrous arsenate of manganese and aluminum, was described as a new species from Nordmark, Sweden, by Sjögren (1884 A). The description of the new species was extended and modified by Sjögren (1884 B; 1885) and Hamberg (1889), the crystal system being variously given as tetragonal, monoclinic and orthorhombic.

Recently Quensel and von Eckermann (1930) described a mineral from Långban, Sweden, which they regarded as a new species and named allodelphite in allusion to the recognized similarity to synadelphite. According to the published descriptions, the two minerals are similar in color, luster and specific gravity; they agree in habit and form; both have slightly oblique extinction; and on *x*-ray powder photographs Aminoff (Quensel and von Eckermann, 1930, p. 643) found that "the lines on the photograms were identical both regarding position and intensity." Chemically the Långban mineral differed from the Nordmark material mainly in carrying 6.23 per cent of silica, which constituent was not reported in the older species; and it was principally on this difference that allodelphite was believed to be a distinct species.

To test this chemical difference an analysis was made by F. A. Gonyer on material from the collection of Långban minerals made by Flink (1926) and acquired some years ago by the Harvard Mineralogical Museum. The specimen used bears Flink's unidentified species number 325, the same number as that attached to the material analyzed as allodelphite by Almström (Quensel and von Eckermann, 1930).[1] The new analysis, as given and discussed later, shows only 1.45 per cent $SiO_2$. Thus the principal ground for regarding allodelphite as a distinct species proves to be false, and we are forced to conclude that the material to which the later name was attached agrees in all essentials with the described characters of synadelphite. This conclusion is confirmed by an examination of several specimens of typical synadelphite from Nordmark which showed crystallographic, physical and optical properties identical with those of the Långban material.

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[1] Dr. Quensel has been kind enough to send a specimen of the Långban mineral described as allodelphite. It has arrived just as this paper is about to go to press. Examination of it shows that it agrees in all particulars with the material in the Harvard collection bearing Flink's No. 325.

## SYNADELPHITE FROM LÅNGBAN

Several years ago Professor Palache measured some crystals (Flink's No. 325) from Långban, and found them to agree in form with allodelphite of Quensel and von Eckermann (1930). A microscopic examination of the crystals by Dr. Berman disclosed the fact that, instead of being homogeneous, they were made up of a nearly colorless interior with a red coating, which appears to be a variety of the material forming the central core. Because this fact had apparently been overlooked by Quensel and von Eckermann, a more complete study of the mineral was undertaken.

*Morphology*. The Långban crystals are small (1–3 mm.), short, striated prisms of orthorhombic appearance with simple terminations. A typical crystal (Fig. 1) has exactly the appearance of the crystal of synadelphite figured by Sjögren (1884 B; 1885). Taking the vertical prism as {110} and the domatic prism as {011}, the observed forms are *b*{010}, *m*{110}, *d*{011}, *p*{121}, of which *m* and *d* are habitually large, *b* and *p* narrow. Two-circle measurements on ten crystals are summarized in Table 1; these lead to the elements and calculated angles given in Table 2.

TABLE 1. SYNADELPHITE: TWO-CIRCLE MEASUREMENTS OF TEN CRYSTALS

| Forms | No. of faces | Measured | | Measured Mean | | Calculated | |
|---|---|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | $\phi$ | $\rho$ | $\phi$ | $\rho$ |
| *b* 010 | 13 | — | 89°57′–90°05′ | 0°00′ | 90°01′ | 0°00′ | 90°00′ |
| *m* 110 | 25 | 61°39′–63°11′ | 89°57′–90°05′ | 62°01′ | 90°02′ | 61°56′ | 90°00′ |
| *d* 011 | 10 | 0 00 – 0 01 | 29 31 –30 29 | 0 00 | 30 30 | 0 00 | 30 20 |
| *p* 121 | 28 | 43 08 –43 41 | 57 40 –58 07 | 43 21 | 57 58 | 43 13 | 58 02 |

TABLE 2. SYNADELPHITE: ANGLE-TABLE

$a:b:c=0.5333:1:0.5851$ $\qquad p_0:q_0:r_0=1.0970:0.5851:1$

$q_1:r_1:p_1=0.5333:0.9598:1$ $\qquad r_2:p_2:q_2=1.7094:1.8751:1$

| Forms | $\phi$ | $\rho=C$ | $\phi_1$ | $\rho_1=A$ | $\phi_2$ | $\rho_2=B$ |
|---|---|---|---|---|---|---|
| *b* 010 | 0°00′ | 90°00′ | 90°00′ | 90°00′ | — | 0°00′ |
| *m* 110 | 61 56 | 90 00 | 90 00 | 28 04 | 0°00′ | 61 56 |
| *d* 011 | 0 00 | 30 03 | 30 30 | 90 00 | 90 00 | 59 30 |
| *p* 121 | 43 13 | 58 02 | 49 30 | 54 30 | 42 12 | 51 51 |

The adopted morphological lattice, which agrees with the structural lattice as determined later, is different from those chosen by the previous observers whose elements and symbols may be transformed to the new setting by the determinants:

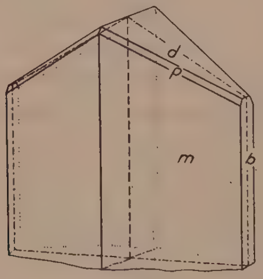
Quensel & von Eckermann to Hurlbut: 010/200/001
Sjögren to Hurlbut: 001/200/010

Due, perhaps, to the similarity in the angles *mm*, *dd*, Sjögren's symbols are evidently in error in that the indices *k* and *l* require to be interchanged. The transformation given applies to Sjögren's uncorrected indices. The fundamental angles of the previous workers are compared with the new measurements in Table 3, which shows that the minerals named synadelphite and allodelphite are morphologically alike.

TABLE 3. SYNADELPHITE: MEASURED ANGLES

| Sjögren | | Quensel and v. Eckermann | Hurlbut |
|---|---|---|---|
| Original | Corrected | | |
| $(100):(120)$ | $=(100):(102)=59°46\frac{1}{2}'$ | $ao=(100):(102)=59°16'$ | $bd=(010):(011)=59°40'$ |
| $(100):(102)$ | $=(100):(120)=61°50'$ | $ai=(100):(120)=62°13'$ | $bm=(010):(110)=61°56'$ |

*Physical Properties.* Megascopically, synadelphite appears to be a red or dark brown mineral, and as such it has been described. However, examined microscopically one can distinguish a nearly colorless interior coated with a thin red film. The mineral, therefore, should be described as pale brown or colorless with a red coating of different material. An imperfect cleavage is present parallel to (010). The specific gravity of the mineral free of coating, as determined by suspension in Clerici solution, is 3.57.



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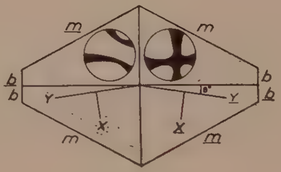

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FIG. 1. Synadelphite. Pseudo-orthorhombic crystal of typical habit.

FIG. 2. Synadelphite. Basal section of a fourling twinned by reflection in (100) and (010). When one pair of parallel individuals are at extinction (stippled), the interference figures in a pair of twinned individuals are as indicated.

*Optical Properties.* Morphologically synadelphite appears to be orthorhombic, but in polarized light the crystals extinguish at a small angle against the vertical axis. Quensel and von Eckermann (1930, p. 640) state, "An angle of extinction in the zone of elongation not exceeding 2° to 3° has been observed in some crystals, but is generally wanting." Hamberg (1889, p. 223) also observed an extinction angle but, nevertheless, called the mineral orthorhombic. Basal sections observed in polarized light show that each crystal is made up of two individuals twinned by reflection in (100) and (010), thus giving a fourling in which the adjacent parts are in twinned relation, while the diagonally opposite parts are in parallel position (Fig. 2). Hamberg (1889, p. 223) also noted such an appearance but did not recognize it as twinning. If one of the principal optical directions coincided with the vertical axis, the observed twinning would indicate a pseudo-orthorhombic monoclinic lattice with the chosen vertical axis as [010]. This is not the case, since on (100), $Z':c[001]=8°$ and on (010), $Z':c[001]=8°$. The lattice is therefore triclinic, twinned by reflection in the nearly rectangular axial planes (100), (010). The optical orientation is shown in the stereographic projection (Fig. 3). The eccentric nature of the interference figures obtained on a twinned basal section is shown in Fig. 2. Since the planes (011) and (010) show no sensible re-entrant angles, the triclinic axial angles cannot differ from 90° by more than a few minutes of arc.

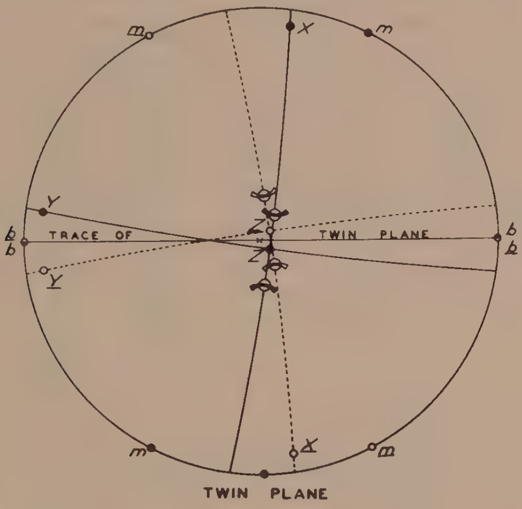

FIG. 3. Synadelphite. Triclinic optical orientation.

The optical elements of synadelphite are as follows:

| | Orientation | | $n$(Na) | |
|---|---|---|---|---|
| | $\phi$ | $\rho$ | | |
| X (colorless) | − 8° | 86° | 1.750 | Positive |
| Y (colorless) | −172° | 86° | 1.751 | 2V=37° |
| Z (light brown) | 42° | 7° | 1.761 | $r>v$ |

Quensel and von Eckermann obtained their values for the refractive indices by the method of minimum deviation, which no doubt accounts for the lack of agreement with those given above. In using a crystal in this manner, the light would pass first through the red coating into the synadelphite, then from one twin individual into the other, and finally emerge through the coating. Any value thus obtained would be false.

*X-Ray Measurements.* With the knowledge that all of the crystals of synadelphite are twinned, great care was taken in breaking out a portion of a single individual for *x*-ray study. A rotation photograph and Weissenberg photographs of the zero and first layer lines were made with $c[001]$ as the axis of rotation. Similar photographs were also taken using a twin crystal; these were found to be indistinguishable from those of the single individual. The two sets of *x*-ray photographs confirm the morphological conclusion that the crystal lattice is sensibly orthorhombic, since there is no visible separation of the *x*-ray diffractions due to twinning.

The dimensions of the unit cell are:

$$a_0 = 9.91\text{Å},\ b_0 = 18.70\text{Å},\ c_0 = 10.65\text{Å}$$

giving $a_0{:}b_0{:}c_0 = 0.5321{:}1{:}0.5695$, which compares with the morphological axial ratio: $a{:}b{:}c = 0.5333{:}1{:}0.5851$. The volume of the unit cell is 1962 cubic Å. The density of synadelphite free of the red coating is 3.57. Hence the molecular weight of the unit cell $M = 4246$.

*Composition.* The existing analyses of synadelphite and allodelphite are listed below, together with a new analysis of synadelphite from Långban.

TABLE 4. SYNADELPHITE AND ALLODELPHITE ANALYSES

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $SiO_2$ | — | — | 6.23 | 1.45 |
| $As_2O_5$ | 29.31 | 32.43 | 21.91 | 26.89 |
| $As_2O_3$ | — | — | 0.62 | — |
| $Sb_2O_5$ | — | — | 0.15 | — |
| $Mn_2O_3$ | 11.79 | — | — | — |
| $Al_2O_3$ | 6.16 | — | 1.50 | 1.41 |
| $Fe_2O_3$ | 1.23 | — | 0.98 | 0.86 |
| FeO | — | 0.17 | — | — |
| MnO | 35.71 | 56.43 | 50.30 | 53.10 |
| CaO | 3.76 | 0.28 | 1.10 | 1.55 |
| MgO | 2.19 | — | 6.22 | 4.62 |
| PbO | — | — | 0.39 | — |
| $K_2O$ | — | — | 0.74 | 0.79 |
| $Na_2O$ | — | — | 0.53 | 0.62 |
| $H_2O$ | 11.39 | 11.33 | 8.82 | 8.52 |
| Insol. | — | 0.19 | — | — |
| | 101.54 | 100.83 | 99.49 | 99.81 |

1. Synadelphite, Nordmark, Sweden; anal. A. Sjögren, in Sjögren (1885).
2. Synadelphite, Nordmark, Sweden; anal. Blix, in Quensel and von Eckermann (1930).
3. Allodelphite, Långban, Sweden (Flink's No. 325); anal. Almström, in Quensel and von Eckermann (1930).
4. Synadelphite, Långban, Sweden (Flink's No. 325), fresh interior of crystals; anal. F. A. Gonyer.

Analyses 1 and 2 were presumably made on the same material; 3 and 4 were made on samples bearing the same specimen number. Since the results all differ considerably, it would appear that the values given were somewhat influenced by impurity of material and analytical difficulties. The most notable difference lies in the $SiO_2$ values in the two analyses of material from Flink's Långban specimens. We are obliged to conclude that the high value reported by Almström is an error and that, therefore, the main chemical difference between synadelphite and allodelphite is fictitious.

Table 5 gives the atomic content of the unit cell of synadelphite from the new analysis (anal. 4, Table 4, reduced to 100 per cent) and the molecular weight, $M=4246$.

TABLE 5. SYNADELPHITE: CONTENT OF THE UNIT CELL

| | | Molecular Ratio | | Atoms per Unit Cell | |
|---|---|---|---|---|---|
| $SiO_2$ | 1.45 | 0.0241 | Si | 1.0 | 1.0 |
| $As_2O_5$ | 26.94 | 0.1172 | As | 10.0 | 10.0 |
| $Al_2O_3$ | 1.41 | 0.0138 | Al | 1.2 | 1.7 |
| $Fe_2O_3$ | 0.86 | 0.0054 | Fe''' | 0.5 | |
| MnO | 53.20 | 0.7500 | Mn | 31.8 | 39.4 |
| CaO | 1.56 | 0.0278 | Ca | 1.2 | |
| MgO | 4.63 | 0.1148 | Mg | 4.9 | |
| $K_2O$ | 0.79 | 0.0084 | K | 0.7 | |
| $Na_2O$ | 0.62 | 0.0100 | Na | 0.8 | |
| $H_2O$ | 8.50 | 0.4744 | H | 40.3 | 40.3 |
| | 100.00 | | O | 88.4 | |

Neglecting $SiO_2$ as an impurity, the numbers in the last column give the content of the unit cell as: $R''_{40}(AsO_4)_{10}(OH)_{50}$ or $10[R''_4(AsO_4)(OH)_5]$, where $R=$ Mn, Ca, Mg, K, Na, Fe''', Al. The composition thus written assumes more water than was found, but it appears to be demanded by valency considerations. From analysis 3, Table 4, Quensel and von Eckermann obtained a similar molecular ratio and attempted to balance the formula by recalculating all the arsenic as trivalent and part of the manganese as trivalent. Since these elements are not found in that state, this does not seem as reasonable as assuming more water. Moreover, from the analysis given by Quensel and von Eckermann, Machatschki (1931) in a discussion of allodelphite and synadelphite likewise assumed additional water to obtain a balanced formula.

## PLUMBOSYNADELPHITE

As previously mentioned, a red material of variable thickness is to be found coating the crystals of synadelphite from both Nordmark and Långban. On examination, the coating proved to be a new variety, to which the name plumbosynadelphite is given. This mineral has a high luster, a hardness of 4 and a density of 3.79.

The optical elements of plumbosynadelphite are as follows:

| | $n$(Na) | |
|---|---|---|
| $X$ (light brown) | 1.851 | Positive |
| $Y$ (brown) | 1.864 | $2V=40°$ |
| $Z$ (dark red-brown) | 1.894 | |

Due to the lack of crystals the crystal system and optical orientation were not obtainable.

It is found that the above-listed optical properties are in good agreement with those given for synadelphite by Larsen and Berman (1934). The specimen of synadelphite, No. 84331 of the U. S. National Museum, on which Larsen originally worked out the optics, was loaned to the writer through the courtesy of Dr. Wm. F. Foshag. Examination of it showed that the synadelphite is covered by an extremely thick layer of plumbosynadelphite, and it was apparently on this coating material that the published optical data were obtained.

$X$-ray powder photographs of both synadelphite and plumbosynadelphite were taken and a comparison of them shows considerable differences, although several of the stronger lines are similar in both position and intensity.

Enough plumbosynadelphite was separated for a chemical analysis. Because of the extremely fine grinding necessary to separate it from the synadelphite, the separation was not complete, and it is estimated that the sample analyzed had 10% synadelphite as an impurity.

Analysis of Plumbosynadelphite by F. A. Gonyer

| | |
|---|---|
| $SiO_2$ | 0.63 |
| $As_2O_5$ | 26.18 |
| $Fe_2O_3$ | 0.48 |
| MnO | 52.27 |
| CaO | 1.25 |
| MgO | 5.89 |
| PbO | 3.24 |
| $K_2O$ | 0.70 |
| $Na_2O$ | 0.59 |
| $H_2O$ | 8.74 |
| | 99.97 |

The above analysis is very similar to that of synadelphite, the only important difference being the presence of 3.24% PbO. Since in specific gravity, optical properties, and structure, as shown by $x$-ray powder photographs, the coating is different from synadelphite, the variety name plumbosynadelphite is proposed for it. With no lead present in the synadelphite itself, it is reasonable to assume that the coating is not merely a surface oxidation of the manganese, as suggested by Sjögren (1885, p. 155), but an alteration accompanied by the deposition of material. Another explanation of the universal coating on synadelphite may be a zoning similar to that found in the plagioclase feldspars, the solutions toward the end of the period of deposition having been richer in lead.

## ACKNOWLEDGMENTS

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## Abstract

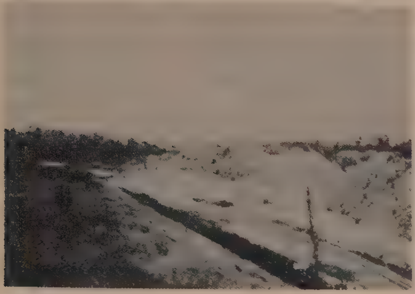
The identity and origin of the clay mineral in the fullers earth from Attapulgus, Georgia, has been studied. Data which have appeared recently in the literature concerning the creation of a new mineral species called "attapulgite" are not verified. *X*-ray diffraction studies, determination of refractive indices and chemical analyses point to the identity of the clay mineral constituent with montmorillonite.

It is believed that the clay represents an accumulation of weathered montmorillonite derived from the crystalline rocks of the highlands. The field relations of the Attapulgus clay, the structure and texture of the clay, and settling experiments lead to the conclusion that the fullers earth beds were accumulated under shallow water. The suspended clay mineral probably settled slowly and built up a mass of more or less flat-lying flakes oriented parallel to the lamination. The clay was probably later subjected to the minor pressure of overlying sediments.

## Introduction

The adsorptive or bleaching clay industry in the United States dates from 1893. At that time it was found that clay from deposits in the vicinity of Quincy, Florida (Van Horn, 1911), could be substituted to advantage for German fullers earth. Fullers earth had been discovered in Arkansas before, as reported by J. C. Branner (1913), but the production of the Arkansas deposits turned out to be of minor importance. Since the original discovery in the vicinity of Quincy, the fullers earth production in the Georgia-Florida district (Shearer, 1917) (Sellards, 1909) has become the most important in the United States. The two largest operating plants are located at Attapulgus, Georgia, and Quincy, Florida, where several hundred thousand tons of clay are produced annually. Large clay pits are operated at Midway and Jamieson in Florida, according to Gunter (1931, 1933), and in addition, fullers earth is produced farther north in Georgia (Shearer, 1917) and farther south in Florida (Grim, 1933).

Beds of laminated clay which are generally described as fullers earth are known in many places in the district. Exposures are greenish gray when moist, but where dry surfaces are developed by stripping and cleaning operations, the clay is frequently light gray or almost white. The beds are found in the Alum Bluff Group, of Miocene age (Cushman, 1932) (Simpson, 1932), occurring in the Hawthorn formation. Strata may form individual members of sufficient thickness for mining, or may consist of thin horizontal layers intercalated between sedimentary beds of a sandy or calcareous nature. Younger Miocene beds (Choctawhatchie formation) overlie the various formations of the Alum Bluff Group, and are separated from the latter by a disconformity. Not only the associated sedimentary beds, but the fullers earth beds themselves may be truncated by the erosion surface. This feature combines with lenticularity to interrupt the continuity in the distribution of the fullers earth strata.



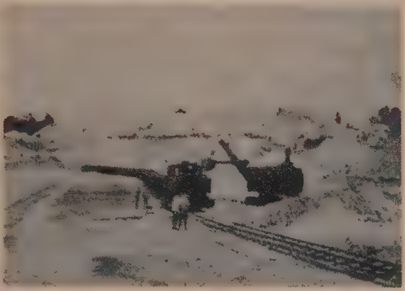
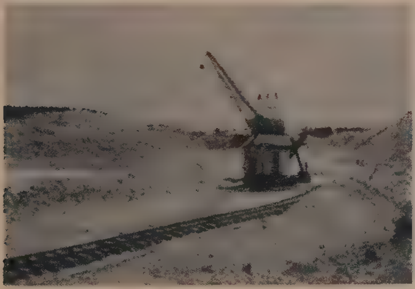


FIG. 1 (left). A general view of the clay workings at Attapulgus, Georgia, showing the large amount of terrane mined in removing fullers earth. The spoil piles of old workings appear in the picture.

FIG. 2 (right). Loading fullers earth at Attapulgus, Georgia. A flat lying bank of fullers earth about ten feet in thickness is shown at the right of the shovel. The bed is also exposed on the opposite side of the workings at the extreme left of the view.

The fullers earth of the Georgia-Florida district has long been known to have well recognized decoloring properties for mineral and vegetable oils, and is used in the oil industry in large quantities. Fullers earth has a high natural efficiency in removing the coloring matter from oil (Nutting, 1933). Oil is allowed to percolate through the clay, during which process a large amount of the coloring matter is removed. Such clays



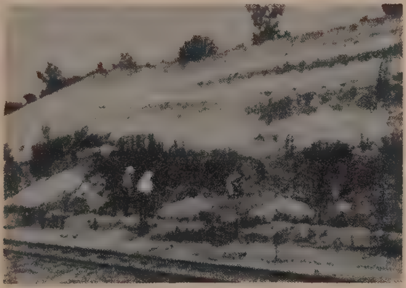


FIG. 3 (left). A stripped bed of Attapulgus clay ready for mining. The steam shovel rests in a depression which represents an old erosion channel on the top of the fullers earth bed.

FIG. 4 (right). Photograph of the fullers earth bed at Attapulgus, Georgia, showing the intercalated sand and clay overburden. The stratum in the foreground about nine feet thick, being cleaned preparatory to taking a sample is fullers earth. A thin streak of precipitated dolomite divides the fullers earth stratum just below the middle.

may be described as naturally active or adsorptive, and are not to be confused with activated adsorptive clays which are acid treated and used in contact filtration. As a rule, the clays which are naturally adsorptive do not respond to acid treatment in suitable degree for use in contact filtration, and the clays which show a high efficiency in the contact process are low in natural adsorption (Nutting, 1932). Two exceptions are worthy of record. A bentonite of natural efficiency, mined at Tehachapi, California, is used in the manufacture of certain types of acid treated clay, according to Kerr and Cameron (1936). Imported acid treated German clay is made by treating a naturally active German fullers earth.

Naturally adsorptive clays are generally marketed under the name *fullers earth*, while acid treated clays are ordinarily marketed under a trade name. Thus far, clays satisfactory for acid treatment have been bentonites, as defined by Ross and Shannon (1926), although many types of bentonite are not satisfactory for acid treatment. The Georgia-Florida clays, although frequently used as standards for comparison in testing the efficiency of a clay for decolorizing purposes, have not as yet been acid-treated on a commercial scale, and are still generally referred to as fullers earths.

Notwithstanding the fact that fullers earth deposits have been worked for many years, and the fullers earth from the Georgia-Florida district has occupied an important position in the field of production of adsorptive clays, there remain many features concerning the nature and behavior of the clay mineral constituent of the fullers earth which merit further study. During the summer of 1936, an opportunity was offered to visit the deposits and collect material for laboratory studies.

Although four deposits were visited,[1] this report is restricted to the clay at Attapulgus, because more time was spent there and a better opportunity was offered to obtain characteristic material. It is felt that a study of the Attapulgus clay is to a large degree applicable to the district, but a more general discussion of the fullers earths throughout the district will be reserved for a later paper.

## ACKNOWLEDGMENTS

The writer wishes to acknowledge the courtesy of Messrs. L. R. Streander and C. M. Schaeffer, of the Attapulgus Clay Co., who made the visits to the clay pits at Attapulgus possible. The kindness of the management of the Floridin Co., of Quincy and Jamieson, and the Fullers Earth Co., of Midway, in permitting a visit to their operations, is also appreciated.

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[1] Deposits operated in the vicinity of Quincy, Jamieson and Midway, Florida.

A number of specimens used in securing x-ray diffraction patterns have been obtained through the courtesy of the U. S. Geological Survey. Dr. Clarence S. Ross of the U. S. Geological Survey has kindly reviewed the manuscript of this paper and offered constructive suggestions. Mr. E. N. Cameron of Columbia University has assisted in portions of the optical and petrographic examinations, and Mr. Earl Emendorfer has made a chemical analysis of the Attapulgus clay.

## COARSE MINERALS IN THE CLAY

The minerals of the fullers earth deposits may be readily divided into coarser fragmental mineral grains and fine clay material. The coarser fragments include quartz, feldspar, and occasional particles of other silicate minerals. The grains are for the most part angular or subangular, and vary in size from a few microns to about 1 mm. in diameter. The more abundant grains encountered in the sandstone associated with the clay include quartz, alkalic feldspar, sphene, magnetite, leucoxene and zircon. Occasional grains of collophane may be observed. Small fragments are distributed throughout the clay and few areas may be found without detrital material, even in thin sections.

The wide distribution of detrital grains throughout the clay indicates similarity of origin for both the grains and the associated clay. Included sillimanite needles in quartz fragments point to crystalline rocks as the original source.

## CARBONATE LAYERS

Carbonate layers are of frequent occurrence in the strata containing the clay. In one place at Attapulgus, a lenticular layer of dolomite varying from 2 inches to 10 inches in thickness, and 100 feet across, has been shown by drill records to extend through the deposits for 1000 feet. The carbonate in this layer is made up of minute euhedral rhombohedra for the most part from 5 to 10 microns in diameter. The crystals are uniform in size and give the appearance of having been directly precipitated. At least it is hard to imagine such uniform crystallization lacking cementing material or the bond of interlocking grains unless produced by direct precipitation. Lenticular deposits of the type observed might be easily precipitated in shallow marine waters.

## "ATTAPULGITE" OR MONTMORILLONITE AS THE ESSENTIAL CONSTITUENT OF ATTAPULGUS CLAY

Descriptions have recently been published by Lapparent (1935), in which the clay mineral constituents from Attapulgus, Georgia, and Mormoiron, France, have been compared, and the conclusion reached that the two are similar hydrous magnesium aluminum silicates warranting description as a separate mineral. The identification has been based upon chemical analysis and *x*-ray diffraction data, and it has been stated that, contrary to the opinion of American authors, the material is not montmorillonite. The name *attapulgite* has been assigned to the mineral (Lapparent, 1936) and a chemical formula derived which indicates an isomorphous series varying between the limits $3SiO_2 2MgO \cdot 4H_2O$ and $5SiO_2 \cdot Al_2O_3 \cdot 6H_2O$. The magnesium end member corresponds to the formula of sepiolite. No known mineral corresponds to the other end member. It is one of the purposes of this paper to review the data available for the identification of the clay mineral from Attapulgus, in the light of recently published descriptions.

Many samples of Attapulgus clay have been examined microscopically and by means of *x*-rays in the course of clay mineral studies over a period of years. Notwithstanding rigorous selection of material in both field and laboratory, and care in the separation of the clay mineral constituent, specimens entirely free from minute microscopic fragments of enmeshed quartz have not yet been secured. *X*-ray diffraction patterns invariably show a few of the more prominent lines due to quartz, superimposed upon an *x*-ray diffraction pattern of montmorillonite.

Numerous *x*-ray diffraction measurements of montmorillonite have been made by different investigators, and a number of these have been recorded in the literature. None of the measurements on record are comparable in accuracy with similar measurements of coarsely crystalline minerals with good reflecting planes. The lines due to montmorillonite are generally too diffused to yield accurate measurements, and too few in number for a wholly satisfactory pattern. Direct comparison of patterns is generally more satisfactory in the identification of montmorillonite than the comparison of computed interplanar spacings with those on record. In the present study and in previous studies of montmorillonite, a standard pattern of montmorillonite has been obtained from specimens from the type locality (Damour and Salvétat 1847). Such material has been available from two sources. Through the courtesy of Dr. Clarence S. Ross, material originally from Montmorillon, France, has been obtained from the U. S. Geological Survey, that was type material received directly from the Museum of Natural History in France. Type material from Montmorillon has also been available from the mineralogical collection of Columbia University.

Early in the course of *x*-ray investigations of the clay minerals, as stated by Bonine (1928), Wherry, Ross and Kerr (1929) reported *x*-ray diffraction patterns of montmorillonite in confirmation of the optical and chemical work of Ross and Shannon (1926). Later Hendricks and

Fry (1930) recorded $x$-ray diffraction measurements of montmorillonite taken with copper radiation in their study of soil colloids. The measurements of $x$-ray diffraction patterns of montmorillonite present in bentonite and fullers earth taken with molybdenum radiation were recorded by Kerr (1931, 1932). At about the same time, Kelley, Dore and Brown (1931) published $x$-ray diffraction measurements of montmorillonite present in soil colloids and in bentonites, obtained with molybdenum radiation. Later Hofmann, Endell and Wilm (1933), in studying the crystal structure and swelling of montmorillonite, gave $x$-ray diffraction measurements of the mineral taken with copper radiation. Further $x$-ray diffraction measurements of montmorillonite taken with molybdenum radiation have been recorded by Laudermilk and Woodford (1934). Gruner (1935) in his study of the structural relationships of nontronites and montmorillonite, has published a series of $x$-ray diffraction measurements taken with iron radiation. Variations in the computation of interplanar spacings, particularly in the case of widely spaced lines, are noticeable in the recorded data. Comparison of the more prominent lines, however, indicates a general agreement in the recorded measurements within the limits of error, when the character of the patterns is considered. Lines and computations considered significant for purposes of comparison are shown in Table 1. In order to make a more definite comparison with the patterns taken with molybdenum radiation, a number of weak lines are omitted, and no reference to comparative intensity is made.

The structure of montmorillonite based on $x$-ray measurements has been interpreted by Dore as being isometric, and by Hofmann, Endell and Wilm as orthorhombic, Gruner, however, has pointed out that a monoclinic structure seems more likely, as would be suggested by the optical properties and probable affiliation with minerals known to be monoclinic. In the case of diffused reflections, usually obtained from atomic planes of montmorillonite, and in the absence of crystallographic data, it would seem that any structural interpretation with the information now available would be largely tentative.

The relationship with sepiolite suggested by Lapparent (1935) is of interest, and it has been considered worthwhile to obtain $x$-ray data on sepiolite for purposes of comparison. Specimens of sepiolite available for study from Hrubschnitz, Moravia; Bear Mt., N. M., and Spain, give identical $x$-ray diffraction patterns, but the patterns in each case fail to agree with montmorillonite. This agrees with the result reported by Ksanda (Foshag and Woodford, 1936), who has also compared patterns of montmorillonite and sepiolite and has found that patterns of the two minerals differ. Also Schaller (1936) has pointed out after a

Table 1

X-ray Diffraction Measurements of Montmorillonite.

| Hofmann,* Endell & Wilm | Hendricks & Fry | Gruner | Dore | Kerr |
|---|---|---|---|---|
| Cu Kα Å | Cu Kα Å | Fe Kα Å | Mo Kα Å | Mo Kα Å |
| 15.2 | | 15.0 | | |
| 4.32 | 4.493 | 4.45 | †5.0 | 4.49 |
| | | | †4.4 | 4.05 |
| 2.50 | 2.551 | 2.535 | 2.56 | 2.48 |
| | | | 1.69 | 1.67 |
| 1.47 | 1.491 | 1.494 | 1.495 | 1.47 |
| 1.27 | 1.286 | 1.285 | 1.295 | 1.29 |
| 1.22 | 1.238 | 1.241 | 1.25 | 1.25 |
| 1.11 | | | | 1.115 |
| 1.02 | | | | 1.020 |
| 0.966 | | | | 0.976 |

* Computed from recorded sin $\theta$.

† Measurements probably too large by about 0.5 A.U.

review of 56 chemical analyses that there is only one sepiolite which has the formula $2MgO \cdot 3SiO_2 \cdot 4H_2O$.

Saponite appears from x-ray patterns to be isomorphous with montmorillonite. The arrangement of lines indicating structural resemblance, but differing in spacing, is striking. Similar x-ray diffraction patterns of saponite have been obtained from material from the Kearsarge and Ahmeek mines (Palache & Vassar, 1925), secured through the courtesy of Professor Charles Palache of Harvard University; from a magnesian bentonite occurring near Needles, California, furnished by Mr. Frank Sanborn of the California State Mining Bureau; and from saponite from Montreal, described by Graham (1918). The interplanar spacings for saponite, nontronite and montmorillonite (or beidellite), members of the montmorillonite group, are given in Table 2. The magnesian clay mineral from Hector, California, described by Foshag and Woodford (1936), also falls in this series but agrees[2] so closely with the spacings for nontronite that the same values are recorded for each. This similarity in x-ray diffraction measurements, however, does not imply chemical similarity, since in this respect the Hector clay differs widely from nontronite.

Drawings of x-ray diffraction patterns of montmorillonite, nontronite and saponite are shown in Figure 5. Care has been taken to reproduce the $x$-ray lines faithfully both in relative position and in intensity.

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[2] Specimen kindly supplied by Dr. Clarence S. Ross of the U. S. Geol. Survey.

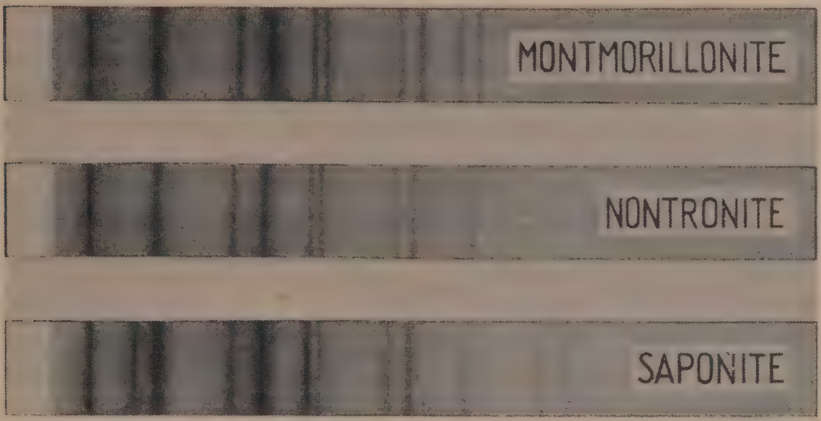


FIG. 5. Drawing of $X$-ray diffraction patterns showing variations in both intensity and spacing to scale.

TABLE 2

$X$-ray Diffraction Measurements in the Montmorillonite Group.*

| Usual Relative Intensity | Saponite A.U. | Hector Clay A.U. | Nontronite A.U. | Montmorillonite (or Beidellite) A.U. |
|---|---|---|---|---|
| S | 4.51 | 4.51 | 4.51 | 4.49 |
| M | 4.06 | 4.05 | 4.05 | 4.05 |
| M | 3.01 | | | |
| S | 2.54 | 2.54 | 2.54 | 2.48 |
| W | 2.45 | 2.45 | 2.45 | |
| M | 1.74 | 1.73 | 1.73 | 1.67 |
| S | 1.52 | 1.49 | 1.49 | 1.47 |
| M | 1.32 | 1.31 | 1.31 | 1.29 |
| M | 1.29 | 1.28 | 1.28 | 1.25 |
| W | 1.155 | 1.145 | 1.145 | 1.115 |
| W | 1.050 | 1.040 | 1.040 | 1.020 |
| M | 1.000 | 0.990 | 0.990 | 0.976 |

* The line at 3.01 A.U. is usually absent or very weak in patterns of montmorillonite, beidellite or nontronite; Mo K$\alpha$ radiation. Letters indicating relative intensities of lines:
S: strong M: moderate W: weak

In the description of attapulgite, $x$-ray diffraction measurements are furnished for 10 lines (Lapparent 1935). Four of these lines may be shown to agree within the limits of error with $x$-ray diffraction lines of montmorillonite. Four agree with lines due to quartz, according to the measurements recorded by Harrington (1927), and confirmed in the present study. Two lines may be due to both quartz and montmorillonite. A likely interpretation of the *x*-ray data is shown in Table 3.

The chemical analysis given by Lapparent is normal for selected Attapulgus clay. For comparison, analyses by Shannon (1926) and Mr. Earl Emendorfer of Columbia University are shown in Table 4.

The analyses indicate that magnesium may be in excess of the amount usually present in montmorillonite. Since Mg may proxy for Al in the montmorillonite group, this excess over the amount in normal montmorillonite may be expected.

TABLE 3

An Interpretation of *X*-ray Diffraction Data for "Attapulgite"

| Interplanar Spacings "Attapulgite" A.U. | Interpretation of Planes Causing Reflections | |
|---|---|---|
| 4.3 | Quartz (4.53) and | Montmorillonite (4.49) |
| 3.25 | Quartz (3.32) | |
| 2.55 | | Montmorillonite (2.48) |
| 2.15 | Quartz (2.12) | |
| 1.8 | Quartz (1.815) | |
| 1.67 | Quartz (1.665) and | Montmorillonite (1.67) |
| 1.49 | | Montmorillonite (1.47) |
| 1.37 | Quartz (1.378) | |
| 1.29 | | Montmorillonite (1.29) |
| 1.25 | | Montmorillonite (1.25) |

The $P_2O_5$ in the analyses is probably due to the presence of a small amount of collophane. Scattered grains of rutile or ilmenite may account for the $TiO_2$ reported. The small amount of $CO_2$ may be due to traces of calcite in the sample analyzed. Probably a small portion of the $SiO_2$, perhaps 3% to 5%, is due to quartz. The alkalies may belong to the montmorillonite, since small amounts are frequently reported.

It seems likely that montmorillonite is responsible for most of the silica, alumina, iron oxide, magnesia, lime and water reported in the analyses. Analyses of montmorillonite from Montmorillon, France, are shown in Table 5.

The indices of refraction of the Attapulgus clay fall within the usual range for montmorillonite, as previously determined by Ross (1926) and as confirmed in the present study. Indices of refraction of the mont-

TABLE 4

Chemical Analyses of Attapulgus Clay

| | Emendorfer | Lapparent | Shannon |
|---|---|---|---|
| Silica | 53.42 | 53.64 | 51.28 |
| Titania | 0.52 | 0.60 | |
| Alumina | 10.06 | 8.76 | 10.56 |
| Ferric oxide | 3.40 | 3.36 | 6.76 |
| Ferrous oxide | 0.18 | 0.23 | |
| Manganous oxide | 0.02 | 0.03 | |
| Magnesia | 9.16 | 9.05 | 10.40 |
| Lime | 1.29 | 2.02 | 1.44 |
| Soda | 0.02 | 0.83 | |
| Potash | 0.64 | 0.75 | |
| Phosphoric anhydride | 0.12 | 0.79 | |
| Water above 110°C. | 9.42 | 10.89 | 20.28 |
| Water at 110°C. | 11.83 | 9.12 | |
| Carbon dioxide | 0.10 | | |
| Chlorine | 0.02 | | |
| Sulphuric anhydride | 0.04 | | |
| | 99.96 | 100.07 | 100.72 |

TABLE 5

Chemical Analyses of Montmorillonite from Montmorillon, France

| | Salvétat | Shannon |
|---|---|---|
| Silica | 49.40 | 48.60 |
| Alumina | 19.70 | 20.03 |
| Ferric oxide | 0.80 | 1.25 |
| Lime | 1.50 | 1.72 |
| Magnesia | 0.27 | 5.24 |
| Manganous oxide | | 0.16 |
| $(K, Na)_2O$ | 1.50 | |
| $H_2O$ | 25.67 | 21.52 |
| | 98.84 | 98.52 |

morillonite in Attapulgus clay were carefully determined by Mr. E. N. Cameron of Columbia University, on air-dried material as follows:

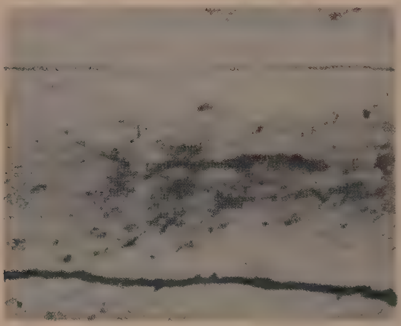
$$\alpha = 1.511 \pm .003 \qquad \gamma = 1.532 \pm .003 \qquad \gamma - \alpha = .021$$

This agrees with the determination by Grim (1933) who gives $\gamma = 1.534$ and $\gamma - \alpha = .022$. The writer has also made index determinations in agreement with the above: $\alpha = 1.510 \pm .003$; $\gamma = 1.533 \pm .003$; $\gamma - \alpha = .023$.

While the magnesium content of Attapulgus clay is greater than is normal for montmorillonite, and the indices of refraction are possibly slightly high, it would not seem feasible to consider the clay mineral constituent of the Attapulgus clay as a distinct mineral with the data now available.

## MICROSCOPIC STRUCTURE OF THE CLAY

Varying degrees of completeness of optical orientation have been observed in all laminated sections of the Attapulgus clay examined, some thin sections showing a much more definite orientation effect than others. Sections of the clay cut parallel to the lamination differ in mass birefringence from sections cut at right angles. It is possible to obtain biaxial interference figures from the matted mass of minute montmorillonite crystals in thin sections cut parallel to the lamination. As would be expected, these sections show little or no birefringence, observed double refraction being limited to occasional crystals of random orientation, or occasional crystals not quite parallel to the plane of lamination. Sections cut at right angles to the plane of lamination (Fig. 6) show maximum birefringence, and have a variable extinction angle, which averages about 10° to the lamination for the slow ray.



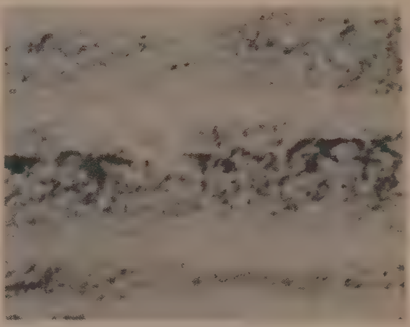


FIG. 6 (left). Attapulgus clay cut perpendicular to the lamination. Thin section photomicrograph, x-nicols (×50). The closely matted clay crystals are sufficiently parallel in orientation to produce uniformity of illumination between crossed nicols. Slight variations in antisotropism may be noted in areas about midway between the laminae.

FIG. 7 (right). Attapulgus clay settled in fresh water. Thin section photomicrograph, x-nicols (×48). The layers in the photomicrograph are due to the rhythmic structure developed by repeated additions of material in forming the filter cake. Individual layers of fine grained material compare favorably in uniformity of orientation with the orientation in the natural clay.

It is believed that the orientation is induced by settling in still water.

It seems likely that the clay particles, in the form of minute flakes, fall in layers. Flakes in the layers not only orient themselves parallel to the surface on which they fall, but also tend to orient themselves parallel to one direction in the plane of the layer. The effect produced amounts to building up a mass of minute flakes of approximately parallel orientation, having to a large degree the properties of a single crystal. In order to obtain optical properties with the microscope, Grim (1934) has allowed montmorillonite to settle in water and build up an oriented cake on a glass slide. The dimensions of the flakes, and the completeness with which the suspended clay material has been broken down into individual crystal units, probably have much to do with the effect. Crystals of montmorillonite are normally so thin that the term *one-dimensional colloid* has been suggested by Wherry (1925).

Several suspensions of Attapulgus clay have been made in the present study, and the suspensions have been collected on a filter paper, a cake of sufficient thickness being built up to allow cutting thin sections normal and parallel to the lamination after drying. A photomicrograph of a thin section of clay collected on the filter paper of a Buchner filter from a suspension in fresh water is shown in Fig. 7. The section is normal to the lamination, and the banding is due to the addition of repeated layers with the separation of finer and coarser particles on settling.

In salt water the clay settles more rapidly but the orientation is not so good (Fig. 8). Pressure applied to the cake formed in salt water increases the orientation effect. Pressure applied to the fresh water cake in a vise while the material is still moist produces packing with pronounced orientation (Fig. 9).

As a result of these experiments, it would seem that settling combined with moderate pressure could account for the formation of the structure in the Attapulgus clay. It is unlikely that the beds have been under any great load, since the overlying strata are inconsiderable. The orientation effect due to settling plus pressure in a vise is about as pronounced as the orientation effect in the natural clay, hence it may be assumed both may contribute to the structure.

Kindle (1932), in describing experiments with the settling of bentonite in water, observed that brine solutions would accelerate the settling and proposed the following interpretation: "This experiment illustrates the possibility that sea water entering a lake near sea level under the special conditions of an exceptionally high tide and extending itself as a separate sheet of salt water would, through the acceleration of settling always produced in very fine sediments by the action of salt, cause the development of a distinct layer along the plane temporarily occupied by the salt water . . . sea border lakes afford opportunities for the interlamination and interfingering of saline and fresh-water sediments." The Georgia-Florida region would appear to offer an ideal illustration of the type of deposition described by Kindle. On the other hand, material allowed to settle slowly in fresh water more nearly duplicates the structure observed in the clay. The imitation is even better when pressure is applied to the settled material. While it would appear that settling and pressure were both effective, the structure suggests that the clay was deposited in fresh water, rather than salt water.

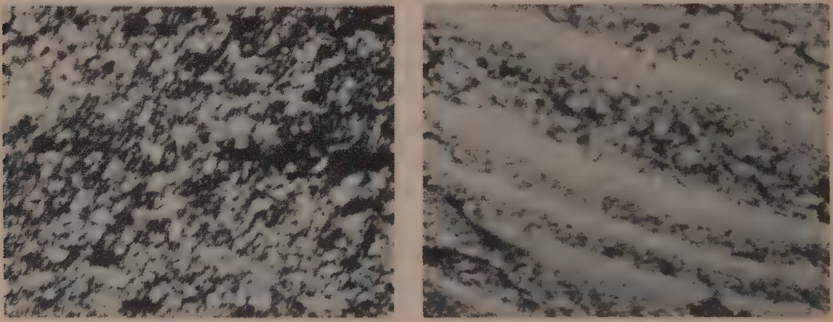


Fig. 8 (left). Attapulgus clay settled in salt water. Thin section photomicrograph, x-nicols (×50). This material shows but a slight tendency to uniformity in orientation. This material settles so rapidly that stratification of the filter cake due to sorting observed in the fresh water settled clay does not develop.

Fig. 9 (right). Attapulgus clay settled in fresh water and pressed. Thin section photomicrograph, x-nicols (×50). The pressure tends to improve the uniformity of orientation.

## Origin of the Attapulgus Clay

The Hawthorn formation in which the Attapulgus clay occurs contains both continental and marine fossils in close proximity to the fullers earth. At Midway, Simpson (1932) has described fossil land mammals which occur both above and below the fullers earth stratum. Cooke (1929) and others have mentioned the occurrence of *Ostraea* and other marine fossils in sandstone strata associated with the fullers earth. Presumably the Hawthorn formation in the vicinity of the fullers earth occurrences represents transitional conditions from marine to continental.

The detrital minerals in the clay, obtained by washing the samples, and the included minerals in the sandy lenses, point to the well-known area of crystalline rocks to the northward as a likely source for the detrital constituents. Since these beds were first described, it has been customary to relate their accumulation to the erosion of the crystallines of the highlands. Recent observations making use of a slightly different technique lead to interpretations in accord with earlier conclusions. This study is more concerned, however, with the role of montmorillonite in the process.

The uniformity of the clay mineral in the Attapulgus clay, and its wide distribution, suggest uniformity of the material deposited. The variable crystalline rocks of the highlands, if unaltered and deposited directly, could hardly be relied upon to furnish material of such uniform nature over wide areas. It would seem more likely that the clay of the lowlands represents an accumulation of a uniform product of alteration or weathering, transported by water and deposited on the old Florida peninsula when the coastal plain sediments were being accumulated.

In view of the widespread occurrence of montmorillonite under a variety of conditions, a brief review of the various origins of the mineral is worthy of consideration, particularly with respect to the occurrence at Attapulgus. Montmorillonite has been reported under conditions suggesting hydrothermal origin. It is probably best established as an alteration product of volcanic glass. It has also been considered to be a product of surface weathering.

Montmorillonite has been found in pegmatites in a number of places. Ross and Shannon (1926) mention such occurrences. Brush and Dana (1880) described montmorillonite from Branchville, associated with soft, partially kaolinized cymatolite and coating cleavage surfaces of partially altered spodumene. A specimen from Branchville in the Egleston Collection, Columbia University, contains montmorillonite as a coating on feldspar. Through the courtesy of Mr. John W. Radu, a specimen of a pink clay from a cavity in a pegmatite at Mt. Mica, Maine, has been secured. The $x$-ray diffraction pattern of this mineral agrees with the $x$-ray diffraction pattern of montmorillonite.

Ewell and Insley (1935) prepared synthetic beidellite by treatment of mixtures of alumina and silica at 350° and 390°C. The beidellite was identified by means of $x$-rays. Montmorillonite has been produced synthetically by Noll (1936) under conditions approaching hydrothermal crystallization in nature. Magnesium hydroxide, aluminum hydroxide, silicic acid and water, confined in a nickel-chromium steel bomb 15 to 24 hours at 300°C. and 87 atm., produced material which Noll described as montmorillonite.

The origin of montmorillonite by alteration of volcanic glass deposited under marine conditions appears fairly certain. Several examples may be found in the bentonite layers of the Monterey (or Modelo) formation of California (Kerr, 1931). Foraminiferal and diatomaceous sediments of great thickness above and below the ash stata point to the deposition of the ash under marine conditions. Relict shards in the bentonite indicate that the alteration to clay followed the deposition of the ash. Evidence is lacking as to whether alteration occurred before or after the deformation of the enclosing sediments.

Unaltered ash, however, occurs at Lompoc, California, in less deformed strata of the Monterey formation, according to Arnold and Anderson (1907). In the diatomite beds at Lompoc, gray volcanic ash occurs interbedded with diatomite in a thin layer about four inches thick. Samples were collected by the writer on a visit to the deposits several years ago. Megascopically, fragments are coarse and granular. Under the microscope, they are clear, transparent and isotropic with $n=1.504$, which according to George (1924) would indicate a rhyolitic ash.

The occurrence of unaltered ash in moderately deformed strata at Lompoc, and of bentonite in highly deformed and crushed strata at Ventura, both in thick marine Miocene sediments, suggests that local conditions subsequent to deposition may have favored the alteration of the Ventura material. Sulphur bearing adjacent or overlying strata, which occur in the Ventura region, may have provided sulphuric acid responsible for the alteration. The broken condition of the strata would accelerate this action.

Wherry (1917) has described clay derived from water-laid volcanic dust, evidently a montmorillonite clay, occurring in a wide area encircling the southern Black Hills of South Dakota. It was Wherry's impression that the dust was altered due to the accompanying gases, including no doubt hydrochloric acid, sulphur dioxide and other chemically active gases from volcanic emanations. However, Wherry mentioned the abundance of gypsum derived from the alteration of calcite by solution of pyrite in overlying shales. Such action is suggested as offering perhaps a more likely agency for alteration of the volcanic glass.

A significant microscopic feature of the Attapulgus clay is the absence of relict structures indicative of volcanic origin. A large number of thin sections of fullers earth from Attapulgus have been examined without revealing a single feature such as a shard, a flow line, a lithic fragment, or some other feature suggestive of volcanic origin.

Montmorillonite has been recorded as a possible product of weathering on a number of occasions. Laudermilk and Woodford (1934) have described montmorillonite being formed from a pegmatite under conditions which they considered to represent weathering. Hendricks and Fry (1930), Kelley, Dore and Brown (1931), and others have pointed to the likelihood of montmorillonite as a constituent of soil colloids. These factors indicate the role of montmorillonite in weathering.

It seems possible to conclude that the Attapulgus clay represents an accumulation of montmorillonite as a weathering product resulting from the decomposition of certain mineral constituents of the crystalline rocks of the highlands. The product of decomposition has been transported as deposited in shallow water along the coast in Miocene time. Although the clay is primarily composed of montmorillonite, it is not bentonite. Commercially a fullers earth, and containing montmorillonite as the base mineral, the clay probably represents a water-deposited accumulation of a weathering product. If the assumptions of Kindle may be applied in this case, the clay was accumulated in salt water. Limited settling experiments, however, would point toward the slower settling in fresh water.

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# PEGMATITES AND HYDROTHERMAL VEINS

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The recognition of hydrothermal mineralization in complex pegmatites has led me to speculate as to whether or not such a phase possibly connects pegmatites with ore-bearing hydrothermal veins. It has been appreciated for some time that both types of deposits are formed from residual magmatic liquids. Is the process of crystallization of a magma from the normal igneous rock stage through the pegmatite and hydrothermal phases continuous or discontinuous?

In seeking a possible solution of these problems I have drawn both upon my own field studies and upon those of others. The subsequent paragraphs review some of these observations, and the theories that have been built upon them. At the close I give what is to my mind the most logical explanation (at the present state of knowledge) of the connection between pegmatites and hydrothermal veins. This is admittedly pure speculation, but if it leads to additional thought and search in the field for pertinent evidence it will have served its purpose. More field studies are particularly needed in regions where the "roots" of ore-bearing veins are accessible.

## Historical Review

The possible relationship between pegmatites and hydrothermal veins has been a subject of discussion for at least 35 years. Various comments made by different authorities during this period are quoted in chronological order in the following paragraphs.

An early contribution on this subject was made by Kemp (1901): "Pegmatites are a more or less pronounced pneumatolitic result of igneous intrusion. Pegmatites grade insensibly into quartz-veins. Quartz-veins not visibly associated with pegmatites are open to the same interpretation unless there is positive evidence to the contrary. On the other hand, pegmatites, although widely developed, are but rarely provided with metallic minerals in notable amounts, and the same is true of the quartz-veins visibly associated with them. But it is also true that many regions of great development of pegmatite-veins are devoid of ore-bearing veins, as, for instance, New England."

Spurr (1902–1903) two years later described the transition from a granite dike through a pegmatite to a quartz vein in southern California. "In a single dike he observed, within the length of not many yards, a complete transition from a fine-grained pegmatite to a typical quartz-vein." Similar observations were made in the Walker river range in northwestern Nevada. A few years later, Spurr (1907) published a theory of ore deposition from which the following appropriate paragraphs are quoted:

"To restate in a different form ideas already explained, it must be understood that after each epoch of crystallization in a rock magma, there remains residual from the crystallized-magma rock a more siliceous and aqueous magma, in which the proportion of water to silica becomes progressively greater, since an increasing amount of silica is deposited at successive stages, but very little water at any stage. Finally there results the highly siliceous and aqueous residual magma from which pegmatitic quartz veins have crystallized. With the progressive increase in silica and water, there is a corresponding increase of certain metals, a fact which is exposed by the final precipitation, in the pegmatites and pegmatitic quartz veins, of such rare metals as tin, molybdenum, tungsten, and gold, in considerable quantity (quite out of proportion to their relative amount in the earth's crust).

"I now submit further that there results from the consolidation of the pegmatites and the pegmatitic quartz veins, practically all the accumulated water in the magma; that with this water is associated a greatly accumulated (concentrated or magmatically differentiated) quantity of the highly mobile and solvent elements such as fluorine, boron, and chlorine, whose presence in granite and pegmatite magmas is shown by such granitic and pegmatitic minerals as tourmaline, mica, and apatite; that much silica is present; and that there are also present many valuable metals, constituting a large portion (in some instances by far the greater portion) of the whole amount contained in the original body of magma.

"I submit that from such a residual magma quartz veins of later origin than the quartz veins closely allied to pegmatites are deposited, and that in them valuable metallic minerals are deposited; that from these veins a further residue results, still fluid under such conditions, but subject to partial consolidation (or to phrase it differently, precipitation) at a later period, under different conditions, involving chiefly a lowering of temperature; and that many successive stages of precipitation follow. . . ."

Singewald (1912), after describing geologic relationships of tin deposits in the Black Hills, the Carolinas, and Bohemia, states: "These occurrences illustrate, therefore, a complete gradation from the tin vein type to cassiterite as a primary constituent in the consolidation of a molten magma." The latter refers to cassiterite in pegmatite.

Spurr (1923) in his book on ore-magmas goes into considerable detail in regard to the relationship between pegmatites and ore veins. He states that "In all these dikes, pegmatite, quartz (feldspar), and quartz, the quartz is of a characteristically easily recognized type—coarsely crystalline, blue-white. It is identical in appearance with the quartz of the deeper-seated gold-quartz veins, as those of the Appalachians and California; . . . ." Farther on he states: "Closely allied to the pegmatites, however, are the pegmatitic quartz veins, in which the segregations of metallic minerals are often considerable and are valuable commercially. These are pegmatites with practically all the non-metallic minerals withdrawn save quartz. They characteristically occur in the vicinity of true pegmatites and show by transition their intimate connection with and derivation from these. They may and often do contain feldspar and other non-metallic pegmatitic minerals, but only in small quantities and as accessory minerals. They evidently represent, in short, a more highly differentiated, more strictly residual pegmatitic magma from which most of the principal granitic constituents save quartz have been separated.

"Closely allied to these metalliferous quartz veins of close pegmatitic affiliation are similar quartz veins not so closely associated with pegmatites and carrying scattered free gold, auriferous pyrite, and other sulphides."

Elsewhere in his monograph he notes that at Silver Peak alaskite pegmatite is "transitional into the gold-quartz veins, and primary free gold was found in this pegmatite."

Niggli (1929) evidently believes that mineral formation is a continuous process from the magmatic stage, which produces igneous rocks, through the pegmatite and pneumatolytic stage to the hydrothermal stage. He refers to the pegmatite and pneumatolytic stage as forming the connecting link between the stage of silicate melts and the aqueous solutions characteristic in the hydrothermal stage. He describes this process as follows: "The residual solutions continuously change in composition, and the melt gradually assumes the character of a pegmatitic, pneumatolytic, and finally hydrothermal solution while progressively decreasing in quantity. If it should be a fact that ore deposits are formed from the residual solutions derived from igneous rock consolidation, these deposits must be regarded as *magmatic formations* no less than the igneous rocks themselves.

"*Magmatic solutions in all their stages, showing a normal and complete sequence of mineral products, are only to be expected under conditions of moderate depth. Below such a medium level the last stages fall out, their contents being 'crowded' into the pegmatitic-pneumatolytic stage. In more superficial levels a similar 'crowding' takes place under hydrothermal conditions; the pneumatolytic stages are missing.*"

Farther on, Niggli refers to deposits containing pyrite, tourmaline and quartz as representing the transition to hydrothermal deposits.

A compilation of quartz veins or dikes of igneous origin has been published by Tolman (1931). He excludes quartz veins that contain metallic ore deposits, but does mention auriferous quartz veins in Victoria, Australia, which are believed to be of pegmatitic origin because of the presence in varying amounts of feldspar, muscovite and tourmaline.

Holmov (1931) after describing the succession of vein formation, which starts with a pegmatite period, in the Duldurga tungsten deposit of Siberia, states: "The gradations from the pegmatite dikes to the quartz veins, the coarse-grained structure of the interlocking wolframite-quartz veins of drusy structure with a simultaneous formation of wolframite and quartz, point to the magmatic nature of the quartz veins presenting the extreme members among the diaschistic rocks of the granite magma. The siliceous magmatic solutions reopened the pegmatite dikes and, in their turn, were again reopened by later siliceous magmatic solutions."

Loughlin and Behre (1933), although admitting the possibility that a few ore minerals may be deposited by pegmatitic solutions, believe that in most instances the ore minerals are later than the pegmatites and come from a deeper source.

"It is sufficient here to recall that in some pegmatites primary crystallization was followed by fracturing and by the introduction of new material which effected replacement of the original minerals by such later minerals as tourmaline, garnet, and cassiterite. Some of these minerals are characteristic of contact-metamorphic and hydrothermal deposits in both siliceous and carbonate rocks, and appear to be the most direct link that connects the after-effects of igneous intrusion with ore deposits; but the likelihood of a distinct interval between the deposition of these minerals and the introduction of sulphides from a deeper source has already been emphasized.

"The transition of pegmatites into massive quartz veins, even where there is no subsequent development of these later pegmatitic minerals, has led some to maintain that there is a continuous transition through these veins into metalliferous veins; but, if any such transitions have been proved, they are extremely rare. The usual structural relations where metalliferous deposits of appreciable size are closely associated with pegmatites show that the metalliferous minerals, especially the sulphides, were introduced at a distinctly later stage than the pegmatitic quartz by solutions derived from a deeper source than that of the local pegmatites. Small amounts of certain ore minerals may admittedly be the end products of the solutions that formed the pegmatite or the late pegmatitic minerals noted above; but their very scarcity, although according with the general sequence of mineral deposition, lends further support to the suggestion that ore-forming solutions in large quantity are derived from a deep source that was developed by further differentiation after the pegmatitic and contact-metamorphic stages."

The Loughlin-Behre hypothesis, however, does not preclude the possibility that the hydrothermal veins may come from much deeper pegmatites.

Emmons (1933) divides pegmatites into two groups, one of which he considers to be closely related to the hydrothermal veins. "With regard to the distribution of pegmatites it is practicable to consider two groups: (1) those that are composed of feldspar, quartz and mica with subordinate metallic minerals, and (2) those of feldspar, quartz, and mica without workable amounts of metallic ores. The first group is formed chiefly in the fractured hood and in the roof region near the batholith. Pegmatites do not form so far above the base of the roof as do metalliferous veins and, as already stated, those that contain metals in important amounts do not extend far below the roof of the batholith or into the part below the hood. The dead line for such pegmatites is probably two or three miles from the contact between the top of the hood and the base of the roof. For the second group of quartz-feldspar-mica pegmatites no dead line can be established. They may be found in essentially all deeply eroded batholiths, even in those that are most deeply eroded. They lie far below the dead line for metalliferous pegmatites and for mineral veins and presumably form at all stages of cooling. All pegmatites that carry important amounts of metals and those mineral deposits that have quartz-feldspar gangue, like the gold lodes of Silver Peak and Passagem, certain tin lodes of Malay Peninsula and the copper lodes of Moonta, are in the roof and hood regions of batholiths. These deposits have strong pegmatitic affiliations although many of them are more closely allied to veins of the deep zone—the hypothermal deposits of Lindgren's classification." In the next paragraph Emmons states that the formation of fractures "continues after the main stage of the deposition of pegmatites with metals, for the pegmatites generally are older than the normal metalliferous veins. Such veins cut pegmatites."

Weed (1933) definitely connects the hydrothermal veins with pegmatites. "As the molten granitic magma is the mother of pegmatite, so the latter gives birth to the highly gaseous fluids which form quartz veins, and most of our primary ore deposits. The great majority of pegmatites are however as barren of ore minerals as most granites." Farther on he states ". . . it is certain that the strictly igneous period ends in the pegmatite stage and the Volatile or Hydrothermal period begins. There is no sharp line between the ores of one period and the other, since the pegmatites connect them . . . ."

Ross (1933) is one of those recognizing a hydrothermal phase in pegmatites. In regard to a possible relationship between pegmatites and ore veins he states: "It is generally believed by petrologists that aplite-forming and pegmatite-forming materials result from the expulsion of residual magma during the late stage of crystallization when alkalic feldspar and quartz are known to be forming in the parent magma. Quartz is also a late mineral, and during the stage of its formation the expulsion of residual material may be a source of the quartz veins and dikes, but quartz forms over so wide a range of conditions that this is probably not the only source of quartz-forming material." A closer relationship is implied by the same writer (1934) in a later article. "Many pegmatites have been modified and new minerals introduced by post-magmatic hydrothermal replacements. Most of these minerals are of a type that show no obvious relation to ore deposits, but the biotite, tourmaline, garnet, other ferro-magnesian minerals, and the sulphides that belong to the later hydrothermal stages of certain pegmatites, are probably derived from the parent magma by the same processes as similar minerals of ore-bearing veins, and indicate a relationship between the hydrothermal processes in pegmatites and ore veins."

Landes (1934), after describing a quartz vein which contains beryl and molybdenite, concludes that "the relationship between beryl and pegmatite is so close that one is justified in assuming that beryl-containing deposits have been formed by pegmatitic solutions. The quartz-molybdenite-beryl vein of Chaffee County, Colorado, which occurs in a region of granite and pegmatite intrusion, is thought to have been deposited by hydrothermal solutions escaping from a deeper solidifying pegmatite. If these conclusions are correct, quartz veins containing beryl may be looked upon as a link connecting pegmatites with normal quartz veins."

A somewhat similar conclusion in regard to quartz veins containing feldspar has been reached by Anderson (1935): "Much has been written of the association in some districts of gold with pegmatites, but the nature and frequency of this association have not been as fully understood as they should be—probably because this pegmatitic phase is often so limited in extent as to pass unrecognized. Yet, in my experience, it is one of the most frequent and most positive signals of the impending death of a quartz vein.

"Study of a great many outcrops in areas where erosion has largely destroyed the horizons in which the gold-bearing quartz veins were formed shows that at and near the top limit of the dike with which they were associated there was a tendency to the local segregation of its component minerals, the feldspar crystallizing separately, often in large pegmatitic crystals, the quartz as irregular quartz veinlets without continuity or persistence. Usually, the range of travel of the feldspar was small, as, once separated from the quartz, it quickly cooled to the temperature of crystallization. Often the gray or white feldspar is not recognized as such, being thought to be simply a different character of quartz. Thereafter the quartz continued upward alone, with its burden of metallic minerals. If the nature of the invaded rocks and the physical condition of the fracturing permitted, it very quickly assumed a definite course and formed a typical quartz vein."

Palache (1935) in describing paragenesis at Franklin, New Jersey, was unable to draw a sharp boundary between minerals formed by pneumatolytic processes in pegmatite contact zones and those deposited by hydrothermal solutions:

"There is no sharp delimitation between the pneumatolytic veins and those of the next or hydrothermal group. Some species of minerals are found in both, but in the hydrothermal group there is less evidence of replacement in the walls, the veins being in general clearly fissure veins.

"The mineralogy of the hydrothermal veins is scarcely less complex than that of the pneumatolytic veins. Many of the minerals, however, were obviously formed at lower temperatures than the pneumatolytic minerals and either farther from the pegmatitic intrusions or during later fissuring."

Lindgren (1936) apparently believes that a continuous process connects the formation of igneous rocks with hydrothermal vein formation. "In intrusive bodies the residual magma is an aqueo-igneous melt of $SiO_2$, $K_2O$, $Al_2O_3$, $Na_2O$, which is in condition to produce pegmatite. Finally, there takes place by fractional crystallization a separation between the silicates and the volatiles. The pressure increases and the volatile extract, still of acid reaction, may escape and is now in condition to attack any minerals it may encounter. 'It is probable these acid solutions are the principal agents of contact metamorphism, of vein formation, of replacement and metasomatism in general.' "

In summary, most of these writers believe that deposition by hydrothermal solutions is continuous with pegmatite formation. A few cite field observations in support of their conclusions. But almost all admit that with few exceptions ore minerals are noticeably scarce in pegmatites. This subject will be covered more fully in the following section.

## ORE MINERALS OCCURRING IN PEGMATITES

Many references are given in the literature to occurrences of metals in pegmatites, but most such occurrences are non-commercial. An outstanding exception is tin which is mined in pegmatites at a number of localities. Lesser exceptions are tungsten, molybdenum, and some of the relatively unimportant rare metals. These last are not included in the following discussion.

I believe that where metallic minerals do occur in pegmatites they have precipitated from hydrothermal solutions that are formed during and by the crystallization of the pegmatite magma. The evolution of this concept has been given elsewhere (Landes, 1933).

The ore mineral of tin, cassiterite, has been found in pegmatites in many parts of the world. Ahlfeld (1936) describes such occurrences in Bolivia, Artemiev (1930) notes the presence of cassiterite in commercial quantities in lithium pegmatites in Siberia, Davison (1930) classifies some of the Cornwall tin deposits as pegmatite, Dunn (1907) has found tin in pegmatites in Victoria, Krusch (1928) reports a similar occurrence in western Spain, and Scott (1932) mentions cassiterite in pegmatites in a district in the Belgian Congo. A few of the many other authors who have found cassiterite in pegmatites include Ferguson and Bateman (1912), Graton (1906), Hess (1933), Singewald (1912), Anderson (1928) and Faribault (1908). Many tin-bearing pegmatites are described by Jones (1925) in his monograph on the tin deposits of the world.

Another metal commonly found in pegmatites is tungsten. This element occurs both with tin and separately. Deposits in Bolivia are described by Ahlfeld (1932), in western Spain by Krusch (1928), and at various localities by Rastall (1918). Hess (1933) describes the occurrence of wolframite and other ore minerals in pegmatites.

Magnetite is abundant in some pegmatites, especially in the New Jersey highlands as described by Bayley (1910) and Palache (1935). Other localities are mentioned by Buddington (1933). Gold has been recorded from a few localities. Occurrences in Utah have been described by Butler (1920), in Nevada by Spurr (1923), in Brazil by Kemp (1901) and Derby (1911), in Victoria by Tolman (1931), and in Dartmoor, England, by Brammall and Harwood (1924). Even platinum has been found in pegmatites in South Africa, as mentioned by Vogt (1930) and Tyler and Santmyers (1931).

Only one sulphide ore mineral, molybdenite, is found in pegmatites with any consistency. Thomson (1918) describes a number of Canadian occurrences. Among other authors who have mentioned molybdenite in pegmatite are Ahlfeld (1936), Buddington (1933), Rastall (1918), Spurr (1923), Landes (1934), and Warren and Palache (1911). Miscellaneous sulphides, such as pyrite, arsenopyrite, bornite, and chalcopyrite, have been described in pegmatites by Buddington (1933), in Southwest Africa by Niggli (1929), in British Columbia by Kemp (1901), in Washington state by McLaughlin (1919), and in California by Graton (1909). Palache (1935) records galena and sphalerite in the Franklin, New Jersey, pegmatites and over a dozen sulphides, arsenides, and native metals among the pneumatolytic products in the pegmatite contact zones.

## CONCLUSIONS

**Tin, tungsten, and molybdenum.**—The important metals which may occur in commercial amounts in pegmatites are practically confined to tin, tungsten, and molybdenum. Considerable field evidence has been amassed that the pegmatite occurrences of these metals imperceptibly merge with typical hydrothermal veins. The source magmas for the ores of tin, tungsten, and molybdenum are very acidic (Hulin, 1929–30). *Granitic magmas produce pegmatites and these in turn produce hydrothermal solutions which may precipitate ores of tin, tungsten, and molybdenum both in the pegmatite and in veins in the country rock adjacent to and for indefinite distances above the pegmatite.*

**Other metals.**—Most ore minerals, such as gold and sulphides, are derived from less acidic magmas (those that crystallize into granodiorite, monzonite, diorite, and varieties of these rocks). These minerals are not found in pegmatites in commercial quantities. One reason for this is that known pegmatites are very scarce in rocks of this type, much more so than is justified by the lesser area of outcrop (compared with granite) of intermediate rocks, including granodiorite. Is this because most of these rocks have not yet been eroded to the level of abundant pegmatites? Or is it because the intermediate magmas for some reason pass through but a very subordinate pegmatite phase before entering the hydrothermal phase?[1] The previously quoted remarks of Anderson (1935) lend support to this theory, for he found the "mother pegmatite" of gold to be so insignificant as to possibly escape recognition in many cases. *Intermediate magmas during their crystallization sequence pass through a minor pegmatite phase before entering the hydrothermal phase. During the latter gold, sulphides, and similar ore minerals are deposited in whatever pegmatites are present, but mainly in hydrothermal veins in the overlying rocks.*

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# DAKEITE, A NEW URANIUM MINERAL FROM WYOMING

Esper S. Larsen, Jr. and F. A. Gonyer, *Harvard University, Cambridge, Mass.*

The new mineral described in this paper was submitted to the writers by Mr. R. W. Rowlands of San Diego, California. It had already been examined and thought to be a new species by Dr. H. C. Dake of Portland, Oregon. The name dakeite is proposed for the mineral in recognition of Doctor Dake's outstanding service in creating popular interest in mineralogy and the other earth sciences.

Dakeite was found in an excavation on U. S. Highway No. 30, near Wamsutter, Wyoming, about thirty miles west of Rawlins. The workmen thought the yellow mineral to be sulphur and paid little attention to it, but a prospector sent a specimen to Dr. H. C. Dake for determination. Doctor Dake found the mineral to fluoresce in the colors characteristic of the uranium minerals and had specimens sent to the writers for identification.

The specimens are gypsite through which are disseminated in considerable abundance rounded to elongated pisolites of dakeite, some of which are as much as a centimeter in diameter. Several of the specimens contain as much as ten per cent of dakeite.

The gypsite is made up mostly of small crystals of gypsum with a little sand and the dakeite. It is no doubt a surface deposit in a semi-arid region and was probably formed by the rise of water solutions to the surface by capillarity, the evaporation of the water and deposition of the dissolved minerals. The amount of dakeite in the gypsite and the extent of the dakeite-bearing gypsite are, according to the description given the writers, both surprisingly large for a uranium mineral. The country rocks in that part of Wyoming are sedimentary according to the available data. It seems probable that the uranium comes from some disseminated uranium mineral in a sandstone, such as the carnotite-bearing LaPlate sandstone of Paradise Valley, Colorado, or the uranium-bearing sandstone near Lusk, Wyoming.

Like many of the secondary uranium minerals, dakeite is green-yellow (Ridgway 27 b) in color. It has a hardness of about 2½ and a specific gravity of 2.51. It occurs in aggregates of micaceous plates that reach a diameter of two millimeters. It has a perfect basal cleavage. Heated in the closed tube it yields abundant neutral water, and on charcoal before the blowpipe it intumesces while giving off water, and leaves a brown infusible residue. Fused with soda it yields a mass that darkens silver.

Dakeite has the following optical properties:

| | $n$ | |
|---|---|---|
| $X$ (very pale yellow), normal to cleavage | $1.489 \pm 0.002$ | Negative |
| $Y$ (pale greenish yellow) | $1.542 \pm 0.001$ | $2V = 5°$ |
| $Z$ (pale greenish yellow) | $1.542 \pm 0.001$ | Dispersion not perceptible |

In ultraviolet light dakeite is strongly fluorescent in a bright yellowish green and in this respect it is much like willemite from Franklin, but its color is a little greener. It is not appreciably phosphorescent. Considering its high uranium content, dakeite is weakly radioactive, indicating a very young mineral, as would be expected from its occurrence in gypsite.

An analysis of dakeite by Gonyer, made on carefully picked material that was found by microscopic examination to be 99% pure, is given in Table 1 together with the molecular ratios and theoretical composition. The state of oxidation of the uranium was determined by dissolving the sample in $H_2SO_4$ in an atmosphere of $CO_2$ and titrating the resulting solution with $K_2MnO_4$.

Table 1. Analysis, Ratios, and Theoretical Composition of Dakeite

| | | Molecular Ratios | | | | Theoretical Composition |
|---|---|---|---|---|---|---|
| CaO | 18.31 | .326 | 3 | × | .109 | 18.9 |
| $Na_2O$ | 7.31 | .118 | 1 | × | .118 | 6.9 |
| $UO_3$ | 30.27 | .105 | 1 | × | .105 | 30.3 |
| $CO_2$ | 13.71 | .312 | 3 | × | .104 | 14.8 |
| $SO_3$ | 9.61 | .120 | 1 | × | .120 | 8.9 |
| $H_2O$ | 19.95 | 1.108 | 10 | × | .111 | 20.2 |
| Insol. | 1.06 | | | | | 100.0 |
| | 100.22 | | | | | |

The composition of dakeite can be written as $3CaO \cdot Na_2O \cdot UO_3 \cdot 3CO_2 \cdot SO_3 \cdot 10H_2O$ or $3CaCO_3 \cdot Na_2SO_4 \cdot UO_3 \cdot 10H_2O$. In the preliminary description of the mineral (Larsen, 1937) the composition was incorrectly given, as the soda had not then been recognized.

Dakeite is easily and completely soluble in acid. It is also completely soluble in water at room temperature (about 20°C.). Considering the composition of dakeite, this is surprising and the constituents must be present in the solution as a double salt, probably with about the composition of dakeite ($3CaCO_3 \cdot Na_2SO_4 \cdot UO_3$). Treated with hot water for fifteen hours at 85°C., dakeite is decomposed and loses to the solution part of its CaO and nearly all of its $Na_2O$ and $SO_4$. One sample lost:

| | |
|---|---|
| CaO | 3.48 |
| $SO_3$ | 9.98 |
| $Na_2O$ | n.d. |
| $UO_3$ | none |

The insoluble part, after drying at 110°C. weighed 62.1 per cent of the original sample and was a very fine-grained mixture of calcite and a yellow uranium compound.

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# A FURTHER STUDY ON THE AGE OF GREAT BEAR LAKE PITCHBLENDE[1]

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A sample of siliceous pitchblende from No. 1 Pit, No. 1 Vein, Eldorado Claim, LaBine Point, Great Bear Lake, N.W.T., Canada, presumably taken from the upper 10 feet of the vein, has been studied by Marble (1936). It yielded the ratio $Pb/U + 0.36\ Th = 0.201$ as the result of the analyses. If this ratio be corrected for the "common" lead content, as deduced from the atomic weight of the derived lead, 206.05, Marble (1934), assuming that a "pure uranium" lead has the atomic weight 206, it becomes 0.193. This yields an age of 1323 million years.

Hecht and Kroupa (1936) have made similar studies on another sample, whose exact location is not known, but which presumably comes from the same vein, and from near the surface. They obtained a ratio of 0.249, and found the atomic weight of the lead to be 206.08. If we also assume in this case that the excess of the atomic weight over 206 is due to "common" lead from some extraneous source, following Baxter and Alter (1933, 1935), we may calculate a "corrected lead ratio" of 0.232 for the sample of Hecht and Kroupa. This value is somewhat higher than the earlier one, but still indicates an early Pre-Cambrian age for the pitchblende, assuming the absence of alteration. Unfortunately no radiograph of the specimen is available, so more definite evidence on this point is lacking.

Recently Mr. Hugh S. Spence of the Canadian Department of Mines has furnished a further sample of pitchblende, labeled: "Specimen of fresh pitchblende (siliceous type) from depth (below 100 feet), 800 ft. section, No. 2 vein, Eldorado Mine, LaBine Point, Great Bear Lake, N.W.T." It was intended to make analyses and also atomic weight studies on this sample, but the latter work has had to be postponed for some years. Accordingly it is felt that though the age determinations are incomplete, the "lead ratio" should be put on record, in case the atomic weight determinations should be done elsewhere.

The specimen showed no sign of secondary uranium minerals at any point on the surface, or after it had been cut. Reports of microscopic studies kindly made by Professor W. H. Newhouse of Massachusetts Institute of Technology, and by Dr. Charles Milton of the U.S. Geological Survey are on file. An autoradiograph of 48 hours exposure, made on both halves of the specimen after it had been sawed down the middle and the surfaces ground flat, is shown in fig. 1. This indicates that while the pitchblende is brecciated, the distribution of radioactive material seems moderately uniform, and there is little evidence of extensive leaching.

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[1] Contribution from the Committee on the Measurement of Geologic Time, Division of Geology and Geography, National Research Council.

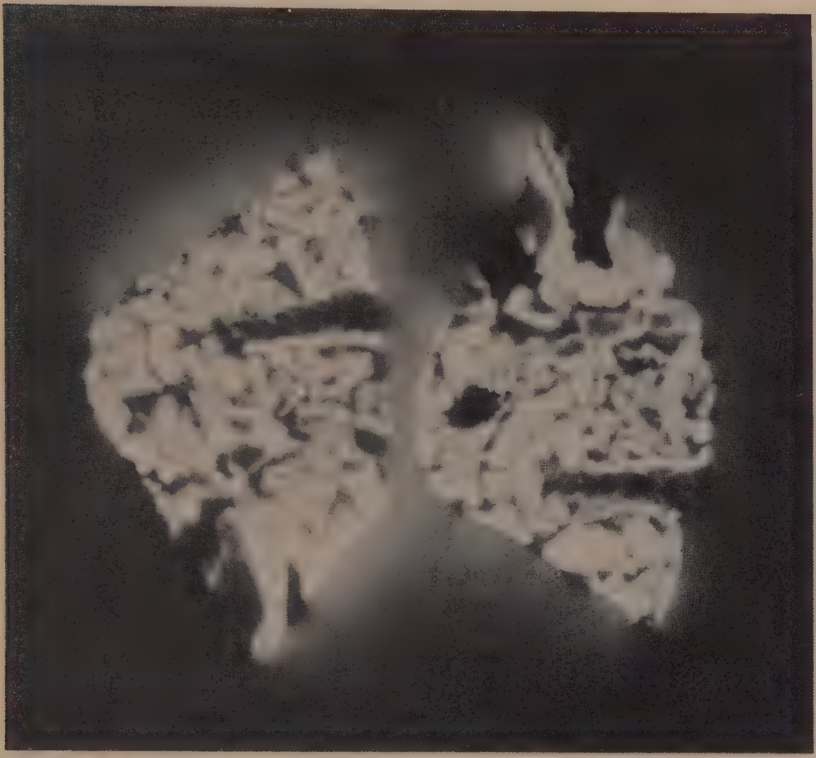

FIG. 1. Auto-radiograph of Pitchblende-Silica Ore, No. 2 Vein, Eldorado Claim, LaBine Point, Great Bear Lake, N.W.T., Canada; 48 hours exposure.

Determinations of lead, uranium, and thorium were made, using previously described methods, with results listed in Table 1.

TABLE 1. ANALYSIS OF PITCHBLENDE-SILICA ORE, NO. 2 VEIN, ELDORADO CLAIM, LABINE POINT, GREAT BEAR LAKE

| Anal. | Wt. Sample | Wt. $PbSO_4$ | ≎%Pb | Wt. $ThO_2$ | ≎%Th |
|---|---|---|---|---|---|
| 1 | 2.40925 gm. | 0.20578 gm. | 5.826 | <0.00008 gm. | <0.003 |
| 2 | 2.69756 | 0.23296 | 5.890 | <0.00007 | <0.002 |
| 3 | 1.18019 | 0.10152 | 5.867 | <0.00010 | <0.008 |
| 4 | 1.16146 | 0.10089 | 5.925 | <0.00015 | <0.011 |

| Anal. | Wt. $U_3O_8$ | ≎%U | Pb/U | Averages |
|---|---|---|---|---|
| 1 | 0.83395 gm. | 29.354 | 0.198 | %Pb= 5.877 |
| 2 | 0.93488 | 29.391 | 0.200 | %U=29.386 |
| 3 | 0.40933 | 29.413 | 0.199 | Pb/U= 0.199 |
| 4 | — | — | — | 5.877/29.386= 0.200 |

As a first approximation, 206.05 has been used for the atomic weight of the lead, as for the earlier sample. Any change in this figure may be expected to be small, and would not affect the analytical results by more than about one per cent.

No correction for the trace of thorium reported is made in the computation of the "lead ratio," as in all cases the tiny, barely weighable residue carried some of the rare earth oxides, as shown by its buff to pale yellow color. The weight of $ThO_2$ reported is thus a maximum. Measurements by other methods on other samples indicate a maximum thorium content of 0.02 per cent, which would affect the "ratio" by not more than one unit in the third decimal. This is no greater than the uncertainty of the other determinations.

The "uncorrected age" calculated from the above figures, using the logarithmic formula of Holmes (1931) and others, is 1368 million years.

A complete analysis of this sample was made, with lead and uranium sought at some point in all other separations, but they could never be detected. An analysis of such a mixture of pitchblende and silica, with traces of other materials, is of insufficient mineralogical interest to warrant publication.

The "lead-ratio" and age calculated therefrom are in reasonable agreement with those found for the first sample studied, and of the same order as those found by Hecht and Kroupa. It should be noted that samples from different veins and different levels yield nearly the same results, thus indicating a general uniformity of the age of the whole ore body, as previously suggested by the writer. These latest figures, bearing out this tentative conclusion, indicate that the Great Bear Lake pitchblende was apparently deposited in early Pre-Cambrian time. The need for further analyses and studies of the isotopic composition of the contained lead is still urgent.

The courtesy of the Assistant Secretary of the U.S. National Museum in permitting the use of the laboratory facilities of the Museum is gratefully acknowledged. Dr. W. F. Foshag and Mr. E. P. Henderson of the Museum, and Dr. R. C. Wells of the U.S. Geological Survey have been of great assistance in many details.

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# SULPHATE INCRUSTATIONS IN THE COPPER QUEEN MINE, BISBEE, ARIZONA

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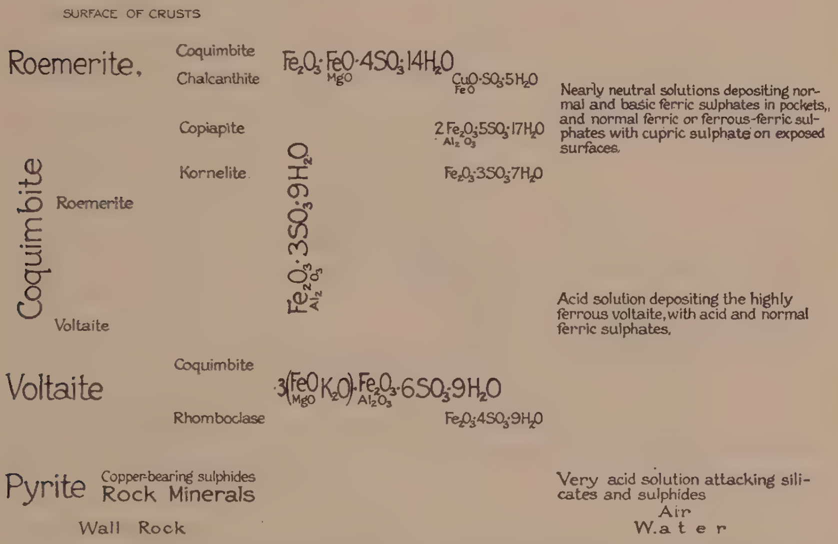
Through the courtesy of Dr. Augustus Locke the geologists of the Phelps Dodge Corporation sent us several incrustations from the walls of the Copper Queen Mine, Bisbee, Arizona. The crusts were described as usually moist but not dripping, and as formed at a temperature of about 32°C. (90°F.). The adherent wall rock is silicified porphyry and minutely impregnated with pyrite and small amounts of copper-bearing sulphides.

The crusts are irregular porous excrescences several inches thick with constituent minerals generally in a grading zonal order. The minerals are sulphates, and four of them typical ferric salts.


SURFACE OF CRUSTS
Roemerite.
Coquimbite
Chalcanthite
$Fe_2O_3 \cdot \underset{MgO}{FeO} \cdot 4SO_3 \cdot 14H_2O$
$\underset{FeO}{CuO} \cdot SO_3 \cdot 5H_2O$
Nearly neutral solutions depositing normal and basic ferric sulphates in pockets, and normal ferric or ferrous-ferric sulphates with cupric sulphate on exposed surfaces.
Copiapite
$2\underset{Al_2O_3}{Fe_2O_3} \cdot 5SO_3 \cdot 17H_2O$
Kornelite.
$Fe_2O_3 \cdot 3SO_3 \cdot 7H_2O$
Coquimbite
Roemerite
$\underset{Al_2O_3}{Fe_2O_3} \cdot 3SO_3 \cdot 9H_2O$
Voltaite
Acid solution depositing the highly ferrous voltaite, with acid and normal ferric sulphates.
Coquimbite
Voltaite
$3(\underset{MgO}{FeO}K_2O) \underset{Al_2O_3}{Fe_2O_3} \cdot 6SO_3 \cdot 9H_2O$
Rhomboclase
$Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$
Pyrite
Copper-bearing sulphides
Rock Minerals
Wall Rock
Very acid solution attacking silicates and sulphides
Air
Water

Theoretically, at ordinary temperatures in presence of water and oxygen, the complete oxidation of pyrite gives acid ferric sulphate which may crystallize completely to the mineral rhomboclase, $Fe_2O_3 \cdot 4SO_3$-$9H_2O$. But in general oxidation of the iron lags behind oxidation of the sulphur, and a mixture is produced of ferrous and ferric sulphates and sulphuric acid. With mineralized wall rock present, the acid brings into solution other bases, which process lowers the acidity of the solutions. From the resulting complex solutions several minerals may form, as shown schematically for these incrustations in the accompanying chart.

Three general sets of minerals are recognized. In the set adjacent to the oxidizing pyrite and the wall rock the minerals are most acid and least oxidized and little ferric iron is present in the surrounding solution; in the set at the surface of the crusts the minerals are least acid (or even basic) and most oxidized and the solutions most concentrated; in the middle set acidity and oxidation are intermediate. Oxidation and acidity are directly related, for ferric iron combines with more sulphate ions than did the ferrous iron from which it was derived. The ferric sulphates here present are known to crystallize from solutions that are more acid than the crystals themselves. Thus the solutions that occasionally drip or flow from the porous crusts carry away some excess acid. A knowledge of the concentrations of acid and ferric oxide necessary for the growth of each of the four ferric minerals aids in an explanatory description of the formation of the other minerals.

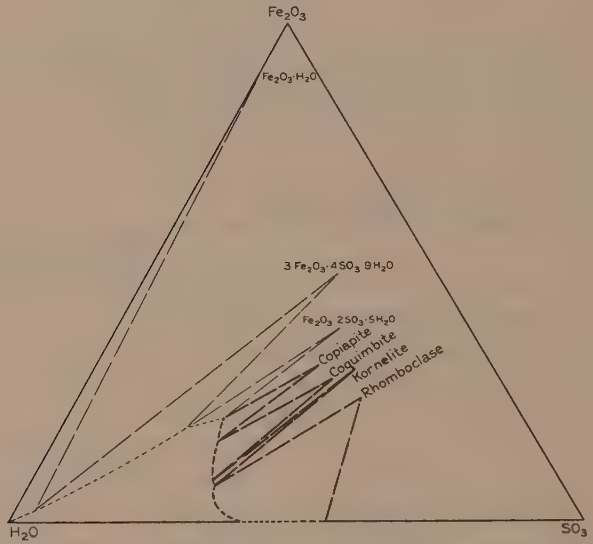


FIG. 1. The system, $Fe_2O_3-SO_3-H_2O$, between 30° and 40°. An extrapolation based on data by F. Wirth and B. Bakke (1914) at 25°, and those of E. Posnjak and H. E Merwin (1922).

The latest of several studies of the synthetic formation of ferric sulphates at ordinary temperatures (25°C.) was made by Baskerville and Cameron (1935)—who give a bibliography—but usually the characteristics of the crystals produced are entirely confined to chemical formulas arrived at indirectly. For temperatures of 50 to 200°C. the crystalline phases are better known—see Posnjak and Merwin (1922). By interpolation, approximate solubility relationships of the various crystalline ferric compounds near the temperatures at which the minerals formed in the mine, are shown in Fig. 1. The clear cuspate area in the lower left represents solutions that are unsaturated. At its dotted boundaries crystals appear, and become more abundant outward. In each wedge-shaped area one crystalline phase, with composition represented by the point of the wedge, is stable in contact with the solutions at the head of the wedge. Only that part of the diagram is now considered that is in bold outline.

Rhomboclase is the least soluble of these sulphates and forms from the most acid solutions. Doubtless this mineral in the incrustations crystallized from solutions near the upper limit of its solubility. Similar ratios of acid to ferric oxide must apply to the accompanying highly ferrous voltaite, for the ferrous and potassium sulphates in solution could affect this condition but little.

Coquimbite is the most abundant mineral of the crusts. Synthetically it was not found at 50°C., but at lower temperatures Scharizer (1906) prepared crystals of normal ferric sulphate, for which an analysis indicated a 9-hydrate, having crystallographic and optical properties characteristic of natural coquimbite. Applebey and Wilkes (1922) considered that their crystals, which T. V. Barker found to be like coquimbite crystallographically, were a 7-hydrate. Analyses of the natural mineral are in poor agreement as to 9 mols. of water. Roemerite, which contains much less ferrous iron than voltaite, is abundant, and forms chiefly under the same conditions as coquimbite: (1) in solution the ratio of acid to ferric oxide is less than for voltaite and rhomboclase; (2) likewise the amount of ferric oxide in solution is greater. Both of these conditions result from oxidation of ferrous sulphate, and from occasional washing away of interstitial acid solution, especially during the early stages of crust formation.

The mineral designated as kornelite is a lower hydrate of normal ferric sulphate than coquimbite. In synthetic experiments it was found to occupy a considerable field at 50°C., and two indirect analyses indicated a 7-hydrate. Identity of the crystals in the crusts with those prepared at 50°C. was established in detail microscopically.[1] At 25°C. Baskerville and Cameron (1935) by indirect analyses of synthetic products having unknown physical properties have inferred an 8-hydrate. The original kornelite of Krenner (1888) was supposed to be orthorhombic and contain $7\frac{1}{2}$ mols. of water. Schaller (1931) has reported a new occurrence of the mineral but has not yet published the details. Larsen and Berman's

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[1] Delicate, very pale violet-colored tufts of laths with twin lamellae parallel to the long thin edges, symmetrical extinctions of 18°; elongation $\alpha$; $\gamma$ normal to plane of flattening; cleavage nearly normal to $\alpha$; $\alpha$ 1.572, $\beta$ 1.548, $\gamma$ 1.639.

(1934) tables list the properties of the mineral essentially like those of the 7-hydrate but give the composition as 8-hydrate. Kornelite is a very minor constituent of the Bisbee incrustations. Solutions only rarely maintain the proper concentrations for its growth, as indicated by a narrow field in Fig. 1.

Copiapite is a basic ferric sulphate, but it also crystalizes from solutions containing more acid with respect to ferric oxide than do the crystals. However, at 50°C., the ratio of acid to ferric oxide in the solution may be either greater or less than the "normal" ratio, $SO_3:Fe_2O_3=3:1$, which may be considered as the neutrality ratio. Copiapites, so called, differ in habit, optical properties, and composition. The causes of the variations have been little studied, but the name should not be applied to a mineral that is not bright yellow in powder unless modification of such yellow by chromophoric substitution can be established.

Chalcanthite occurs in the outer parts of the crusts. It is but a small proportion of the total incrustation, and its presence is due to concentration of copper in the solutions as they approach the evaporation surface.

These processes of crust formation may now be contrasted with processes of leaching near the surface of the ground of oxidizing pyritic ore bodies. As solutions such as those already described begin to accumulate around pyrite which is oxidizing in a rock matrix, two other processes are active; one is the lowering of acidity by reaction with bases of the rock, and the other is intermittent dilution. These processes lead to the formation of jarosites which are analogues of the basic salt $3Fe_2O_3\cdot 4SO_3\cdot 9H_2O$ of Fig. 1[2] and through them—or directly—to the usual ultimate product, a limonitic form of goethite, in the "iron hat" overlying the pyritic ore body.

In measuring indices of refraction of immersed grains, the matching for the apparent principal indices was checked by using a very narrow beam of light incident at all the angles in the chief plane of extinction that the objective would admit. Use was made of a sliding diaphram with a single aperture about 0.5 mm diameter as close as possible to the open condenser iris.

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[2] Baskerville and Cameron (1935) state that solutions containing 26.4 per cent $SO_3$ deposit at 25°C. one continuous series of solid solutions between ferric oxide probably somewhat hydrated and the other probably approaching in composition the basic salt $Fe_2O_3\cdot 2.5SO_3\cdot 7H_2O$. According to the model for the system, $Fe_2O_3-SO_3-H_2O$, between 200 and 50°C., Posnjak and Merwin (1922), it seems more than improbable that the fields of stability of the more basic salts, would almost suddenly—over a 25°C. interval—be transformed into a single field for a single series of solid solutions. The interpretation of Baskerville and Cameron does not appear to follow necessarily from their data.

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# A NOTE ON THE MORPHOLOGY OF MONAZITE

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## Introduction

In connection with some work on Swiss monazites (turnerites) a general statistical analysis of the mineral's morphology was carried out; it is proposed here to summarize and discuss briefly the results obtained. The investigation was made on the published drawings of monazite crystals, most of which are reproduced in Goldschmidt (1920). Several figures are, however, not included in the atlas or have been published subsequently and are contained in papers by Lacroix (1915; 1918; 1922), Palache, Davidson and Goranson (1930), Schoep (1930), Sekanina (1933), Thoreau, Breckpot and Vaes (1936), Ungemach (1916), Wherry (1919). In all 133 figures were examined and 127 of these were found suitable for statistical purposes.

Forty-two forms were identified on the drawings and of these 38 are quoted by Goldschmidt (1920) while 4 come from newer publications as follows: $p=(211)$, contained in Goldschmidt (1897), deleted by him in 1920, found on a crystal from Madagascar by Ungemach (1916); $\Delta=(122)$ and $U=(\bar{1}13)$ found by Ungemach on crystals from Madagascar; $\Phi=(\bar{3}02)$ found by Sekanina (1933) on a Moravian crystal. This author also gives $S=(102)$ but does not figure the form. The letters attached to these forms have been added by the present writer. Eight forms quoted by Goldschmidt (1920) were not found in the drawings. They are the following: $\chi$, $\pi$, $\Gamma$ $v$, $\phi$, $\Sigma$, and two doubtful forms.

## The Forms and Their Persistence

According to Niggli (1922) the most satisfactory method of assessing the importance of a form is to determine the degree of its persistence on the crystals under varying conditions of development. For this purpose as many different crystals as possible must be examined and a selection of individuals made, such that every available combination of forms is represented once and once only. If $D$ be the total number of these (different) combinations and $d$ the number containing the given form, the persistence $P$ of the latter is expressed by

$$P=\frac{d\cdot 100}{D}\cdot \qquad (1)$$

The monazite crystals shown in the drawings examined belonged to 99 different combinations, varying in complexity from 2 forms ($a$-$v$ on crystals from Söndeled, Norway) to 16 forms (on crystals from "Mont

Sorel," Floitental and the Tavetsch valley). The greatest variety of combinations was found when 8 forms are present, though nearly as many variations occurred with 4, 5, 6 or 7 forms. A maximum comprising 55% of the total number of combinations is, therefore, reached between 4 and 8 forms. This corresponds to the observations made on other minerals, which nearly always show their greatest variability in the moderately complicated combinations. It may be added that the individual combinations most frequently met with were *a-b-e-m-w-x* and *a-m-r-v-w-x*.

The application of equation (1) to each of the 42 forms resulted in the values given in the third column of Table 1, which is arranged according to decreasing values of $P$. It will be seen that $a=(100)$ occupies a rather isolated position with the extremely high value $P=97$, and that 16 units separate the form from $v=(\bar{1}11)$ the next highest. The latter is one of a group comprising *v*, *m*, *x*, *e*, *w*, *b*, whose $P$-values gradually decline to 60.

TABLE 1

| Letter | Symbol | $P$ | $S$ | I | II | III |
|---|---|---|---|---|---|---|
| *a* | (100) | 97 | 97 | 93.5 | 4 | 2.5 |
| *v* | $(\bar{1}11)$ | 81.5 | 65.5 | 29 | 39 | 32 |
| *m* | (110) | 75.5 | 68 | 32 | 33.5 | 34.5 |
| *x* | $(\bar{1}01)$ | 72.5 | 72 | 36 | 43.5 | 20.5 |
| *e* | (011) | 65.5 | 59 | 19 | 38.5 | 42.5 |
| *w* | (101) | 63 | 73 | 40 | 39 | 21 |
| *b* | (010) | 60 | 61 | 23 | 36.5 | 40.5 |
| *u* | (021) | 46 | 49.5 | 13.5 | 21.5 | 65 |
| *z* | $(\bar{3}11)$ | 39 | 44 | 0 | 32.5 | 67.5 |
| *r* | (111) | 37 | 53 | 12.5 | 33.5 | 54 |
| *l* | (210) | 27.5 | 45.5 | 0 | 36.5 | 63.5 |
| *c* | (001) | 25.5 | 59 | 24 | 28 | 48 |
| *o* | $(\bar{1}21)$ | 22.5 | 41 | 0 | 23 | 77 |
| *i* | $(\bar{2}11)$ | 22.5 | 37 | 0 | 11.5 | 88.5 |
| *g* | (012) | 18.5 | 36.5 | 0 | 9 | 91 |
| *n* | (120) | 9 | 44.5 | 0 | 33 | 67 |
| *y* | (310) | 9 | 36.5 | 0 | 9 | 91 |
| *s* | (121) | 5 | 37.5 | 0 | 12.5 | 87.5 |
| *d* | $(\bar{1}12)$ | 4 | 33.3 | 0 | 0 | 100 |
| *f* | (112) | 3 | 33.3 | 0 | 0 | 100 |
| *t* | $(\bar{2}12)$ | 3 | 33.3 | 0 | 0 | 100 |

At this point another sharp drop of 14 units marks the transition to a further group consisting of *u*, *z*, *r*, *l*, *c*, *o*, *i*, *g*, which show $P$-values between between 46 and about 20, while all other forms have $P$-values below 10 and in very many cases show the lowest figure (1 combination). A comparison of this sequence with those found on other minerals (see, for instance, the data collected by the present writer, 1930) shows that while the forms very generally tend to separate into groups, the size of these and their position in the scale of *P*-values vary somewhat and thus constitute individual features of each mineral. The highest group, containing what Niggli (1923) has called the characteristic key-forms ("Leitformen"), is for monazite reduced to the one very typical and constantly recurring form *a*=(100). The second group may be said to contain the chief auxiliary forms, one or more of which accompany *a* in the majority of the combinations, while those of groups three and four may be referred to as supplementary and incidental forms respectively. Whereas the former are still fairly widespread, the latter are of exceptional character and mostly restricted to some few individuals. It is interesting to find *r*=(111) and especially *c*=(001) among the supplementaries and ranking among forms with slightly complex symbols. On the other hand all the highly persistent forms have simplest indices and are in this respect unusually homogeneous.

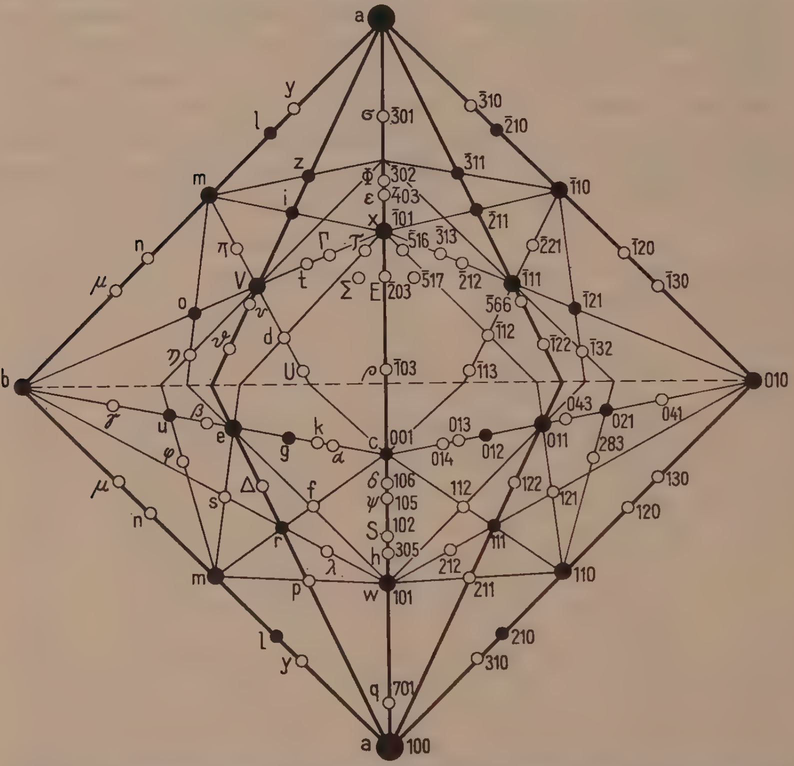

FIG. 1. "Triangular" gnomonic projection of the monazite forms. The persistence of the forms and the importance of the zones is indicated by the thickness of the points and lines.

These facts are brought clearly by figure 1 which is a gnomonic projection of the triangular type advocated by Niggli. The construction was carried out on the principles recently suggested by the present writer (1936) and the plane of projection so chosen that the fundamental triangle is right-angled and isosceles. This enables the triangles representing each quadrant to be fitted together, with the result that a figure is obtained showing similar distribution of the faces as the stereographic projection while preserving the zone-lines characteristic of the gnomonic. The forms are marked in various sizes according to their persistence and various zones have also been drawn and their importance indicated by lines of different thickness. The method adopted for grading the zones was to form the sum of the persistence-values of the forms occurring in each one.

$$Z = \Sigma P. \tag{2}$$

The application of this equation results in the values collected in Table 2 and reveals a distinct maximum for [011] with $Z = 346$. [001] and [100] follow and six other zones have values over 200. All others are of lesser importance.

TABLE 2

| Zone | Number of forms | $\Sigma P$ |
|---|---|---|
| [011] | 10 | 346 |
| [001] | 7 | 279 |
| [010] | 14 | 270 |
| [111] | 7 | 246 |
| [112] | 6 | 244 |
| [101] | 6 | 240 |
| [$11\bar{1}$] | 7 | 231 |
| [110] | 8 | 228 |
| [100] | 10 | 220 |
| | 75 | |
| deduction for forms counted more than once | 25 | |
| | 50 | |

The projection shows that in spite of the rather pronounced obliquity of the axial cross ($\beta = 103°40'$)[1] the general distribution of the forms and zones is a markedly regular one and possesses a distinct similarity to certain cubic projections. This is partly due to the approximation to cubic angles resulting from the axial ratio $a:b:c = 0.9693:1:0.9256$ (metrical pseudosymmetry) and partly due to the peculiarities of the form-selection. It will be noted, however, that the distribution shown by forms of similar persistence and zones of similar importance conforms less well to that required by cubic pseudosymmetry. The high and somewhat isolated *P*-value of the pinacoidal form *a*=(100) and the fact that the chief zones converge in this form introduce tetragonal traits into the projection, which indeed rather closely resembles the type-projections given by Niggli (1926) for the "tabular" mode of that morphological group. The morphology of monazite may, therefore, be described as belonging to the hypocubic type with distinct tendencies towards the last named mode. It may be noted that these relations are best brought out by the setting first chosen for the "turnerite" crystals from the alpine localities, according to which the pinacoids *a*=(100) and *c*=(001) of Dana's monazite setting were interchanged. Figure 2 is a stereographic projection orientated in this fashion, and the pseudosymmetric features referred to above come out very clearly.

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[1] This is clearly shown in the projection by the eccentric position of $c = (001)$.

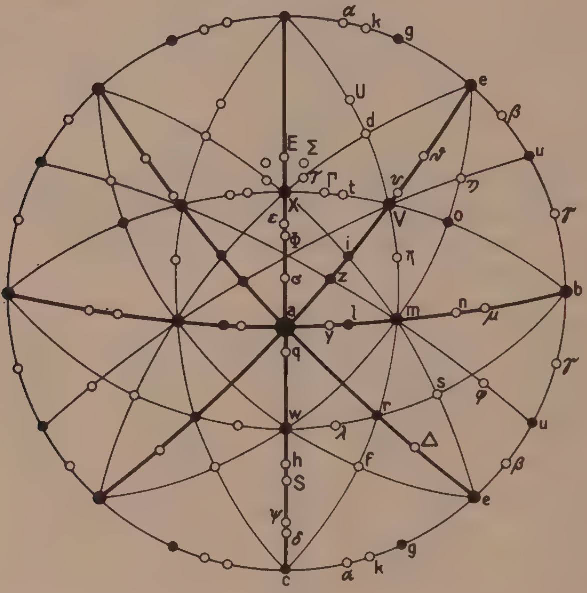

FIG. 2. Stereographic projection of the monazite forms. The mineral is set with the *a*-axis vertical to bring out the pseudo-tetragonal form development.

## THE SIZE-RELATIONS OF THE FORMS

If the forms present in each drawing be divided according to size into three groups, I (large), II (medium) and III (small), three characteristic numbers, *r*, *s*, *t*, may be calculated for each form showing how often on the *n* crystals examined it appears in each group respectively. According to Goldschmidt (1923) the relative size of each form can then be expressed by a number $G$ such that

$$G=\frac{100\,(3r+2s+t)}{3n}. \tag{3}$$

It may be pointed out that this number does not furnish a wholly satisfactory expression for the size-relations because it is not independent of the frequency of the forms. Thus, if on 100 crystals two forms have $r=30$, $s=30$, $t=30$, and $r=20$, $s=20$, $t=20$, respectively, the two $G$-values work out to 60 and 40 respectively, in spite of the equal distribution among the three groups which obtains in each case. A better insight into the size-development of each form is given by the quotient

$$S=\frac{100\,(3r+2s+t)}{3\,(r+s+t)} \tag{4}$$

which gives values lying between 100 (group I only) and 33.3 (group III only) and for cases such as those given above works out to 66.6 quite independently of the frequency. For graphical purposes the three expressions:

$$\frac{100\cdot r}{r+s+t}\,; \quad \frac{100\cdot s}{r+s+t}\,; \quad \frac{100\cdot t}{r+s+t}$$

may be calculated for each form. As the sum of the three terms is always 100, triangular coordinates may be used for plotting and a point in the diagram assigned to the form which at once shows the distribution among the three groups. This has been carried out for the important forms of monazite in figure 3, while the $S$-values are quoted in the fourth column of Table 1.

The most conspicuous fact that emerges is the completely isolated position of $a=(100)$ which very rarely appears except in group I and in the great majority of the crystals considered is a dominant form. The estimation of importance according to persistence and size leads here to the same result, but this is only partly true as regards the other forms. Thus the group of auxiliary forms, though as a whole ranking next in the order of $S$-values and forming a typical group in the centre of the diagram, shows some very marked changes in sequence, the position of $w=(101)$, for instance, being noticeably higher than before. The supplementary forms again appear as a group and occupy the field around pole III of the diagram, but here also the order is changed and $c=(001)$ and $r=(111)$ occupy considerably higher positions by size than by persistence. Nearly all the incidental forms appear exclusively in group III and therefore concentrate on that pole. They are omitted from the diagram.[2]

These indications may suffice to prove that while certain connections do, evidently, exist between the persistence and size sequences, they are of no very precise character and hardly go beyond the general grouping of the forms discussed above. Results obtained by similar methods on other minerals quite bear out this conclusion though the use of $G$-values as a basis of discussion has often tended to obscure the facts. These values being dependent both on persistence (or frequency) and size may, perhaps be appropriately used to strike a mean between the two corresponding sequences and according to them the monazite forms appear in the following order: $a-x$, $m$, $v$, $w-e$, $b-r$, $u$, $z$, $c$, $l$, $o$, $i$, $g$, $n$, $y$, $s$, etc.

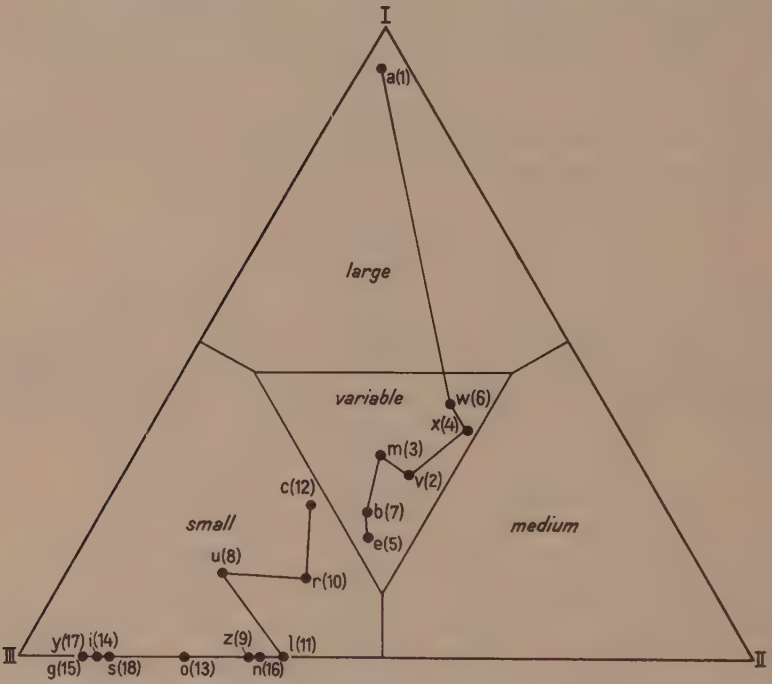

FIG. 3. Size-relations of the monazite forms. The numbers in brackets give the positions of the forms in the sequence of persistence-values.

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[2] A few of these forms do, however, possess high $S$-values, which show that although of extreme rarity they have been observed with large faces. They are the following: $h=(305)$, Binnental by Trechman; $\delta=(106)$, Madagascar by Duparc; $\epsilon=(\bar{4}03)$ and $\beta=(043)$, Madagascar by Lacroix; $\Phi=(\bar{3}02)$, Moravia by Sekanina; $\rho=(\bar{1}03)$, Queensland by Anderson.

When viewed from the standpoint of pseudosymmetry, figure 3 bears out the results previously obtained in a rather remarkable way. The three pseudoequivalent forms, $w=(101)$, $x=(\bar{1}01)$, $m=(110)$, which represent the tetragonal form (101) are quite close together in the diagram, as are $b=(010)$ and $c=(001)$ representing the pseudoprism (100). The form $e=(011)$, which represents the prism (110), occupies a position close to *b*. These facts show that the pseudosymmetry may be expected to manifest itself in the habit of the mineral, and an inspection of the drawings at once brings a number of such cases to light. Thus crystals are often found on which *a-w-m-x* are simultaneously present in dominant development and the similarity to a tetragonal combination can then be a very marked one. The group *a-b-c* is much rarely dominant though Lacroix (1922) has given a typical case of this sort. The group $a$-$b$-$e\pm c$ is a further group which is frequently well developed on the crystals and can also produce tetragonal habit. Although Miers has described a crystal from Cornwall, which besides *a* and other forms shows *v* and *r* in a development suggesting the pseudoform (111), these two forms are widely separated in the diagram and rarely combine in this way. Instead the two forms *a* and *v* often produce crystals of pronounced prismatic habit which like the very frequent case of dominant *a-x* (prismatic with elongation after [010]) and some others must be considered as highly typical for the mineral though lacking the pseudosymmetric character discussed here.

## SUMMARY

A statistical analysis of the form-development of monazite by persistence and size brings out the dominant role of $a=(100)$ and establishes sequences for the other forms which are broadly speaking similar though by no means identical for the two methods of approach. The results indicate that the morphology of monazite is of a hypocubic type with a distinct tendency towards the tabular mode of the tetragonal group.

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# TWO-CIRCLE CALCULATION IN THE HEXAGONAL SYSTEM

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Recently the writer had occasion to demonstrate to a class the coordinates that must be used to locate the indices $21\bar{3}1$ in a gnomonic projection of a hexagonal crystal, showing that this meant measuring two fundamental units on the positive end of the $a_1$ axis, one unit to the right parallel with the $a_2$ axis, and three units in a negative direction parallel to the $a_3$ axis, with the height of the plane of projection above

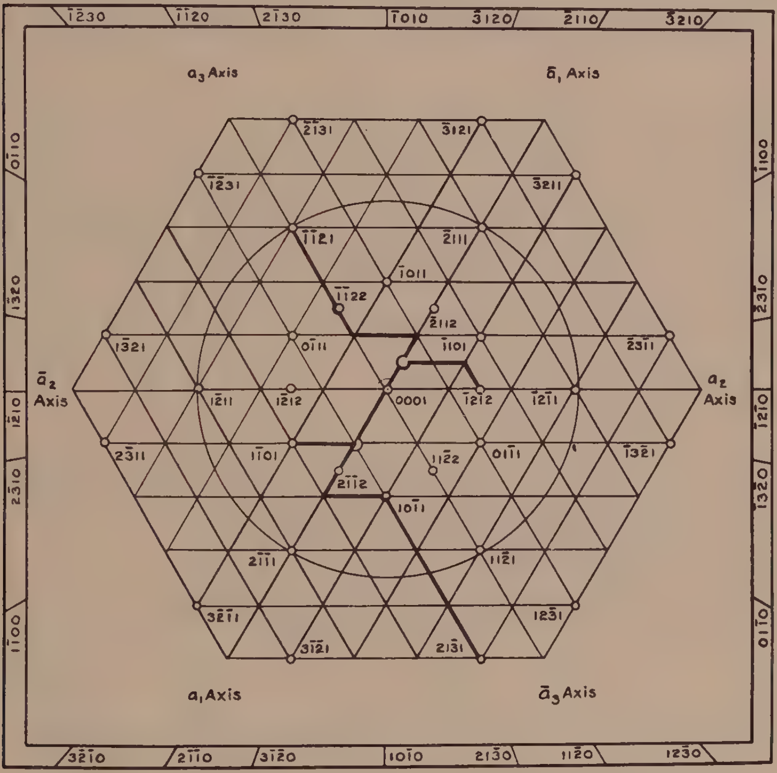

FIG. 1. Gnomonic Projection of Beryl showing *h/l*, *k/l* and *i/l* for the faces $1\bar{1}01$, $21\bar{3}1$, $\bar{1}2\bar{1}2$ and $\bar{1}\bar{1}21$.

the centre of the sphere of projection as the last index of unity. When this was done he noticed that he had located a point which in the terms of Goldschmidt's $pp_0$, $qp_0$ was to be indicated as 41 which is supposed to have the Bravais indices $4\bar{1}\bar{5}1$.

Further observation showed that in every case there is an intimate relation between Goldschmidt's co-ordinates $pp_0$ and $qp_0$ and the Bravais indices $hkil$, which is quite different from what he and all his pupils have thought, for when these indices are given their proper signs and when $h>k>i$,

$$pp_0=\frac{h-i}{l}\,p_0 \quad \text{where } h \text{ and } i \text{ have different signs}$$

and

$$qp_0=\frac{k-i}{l}\,p_0$$

and

$$p_0=\tfrac{2}{3}c.$$

In the accompanying gnomonic projection (Figure 1) of some of the common forms found on beryl a graphical determination of $p_0$ has been made and the indices for the faces $\bar{1}\bar{1}21$, $\bar{1}2\bar{1}2$, $1\bar{1}01$, and $21\bar{3}1$ are indicated as co-ordinates, with the proper signs, in heavy lines, giving in each case $\frac{h}{l}\,p_0$, $\frac{k}{l}\,p_0$, and $\frac{i}{l}\,p_0$.

The following table shows the Bravais symbol for each of these faces together with the proper arrangement of the indices to give the co-ordinates on the three axes.

| Bravais | Indices | | | | Co-ordinates | | |
|---|---|---|---|---|---|---|---|
| | $a_1$ | $a_2$ | $a_3$ | | $a_1$ | $a_2$ | $a_3$ |
| $\bar{1}\bar{1}21$ | $\frac{\bar{k}}{l}$ | $\frac{\bar{i}}{l}$ | $\frac{h}{l}$ | = | $\bar{1}p_0$ | $\bar{1}p_0$ | $2p_0$ |
| $\bar{1}2\bar{1}2$ | $\frac{\bar{k}}{l}$ | $\frac{h}{l}$ | $\frac{\bar{i}}{l}$ | = | $\frac{\bar{1}}{2}p_0$ | $\frac{2}{2}p_0$ | $\frac{\bar{1}}{2}p_0$ |
| $1\bar{1}01$ | $\frac{h}{l}$ | $\frac{\bar{k}}{l}$ | $\frac{i}{l}$ | = | $1p_0$ | $\bar{1}p_0$ | $0p_0$ |
| $21\bar{3}1$ | $\frac{k}{l}$ | $\frac{i}{l}$ | $\frac{h}{l}$ | = | $2p_0$ | $1p_0$ | $\bar{3}p_0$ |

Inasmuch as we must consider positive and negative indices, and positive and negative axes, a complete calculation for a hexagonal crystal should determine the sign and position of all three of the co-ordinates for each and every face. To accomplish this, after the unit first or second order pyramid has been selected by means of the information gained from a gnomonic projection, attention must be paid not only to $\varphi$ and $\rho$ but to the sectant in which the face lies and the positive or negative character of sin 60° which appears as the divisor in securing $pp_0$ and $qp_0$. In order to obtain the proper signs and positions for the co-ordinates, angle $\varphi$ should be measured clockwise and 60°-$\varphi$ counter-clockwise, in which case $\varphi$ may be greater than 30° but not greater than 60°.

In the calculations under these conditions sin $\varphi$, sin 60°-$\varphi$ and tan $\rho$ are always positive but the divisor in the fundamental equations, sin 60°, is positive when the hypothenuse is parallel with the positive end of an $a$ axis, and negative when the hypothenuse is parallel with the negative end of an $a$ axis.

With the introduction of positive and negative signs for the indices we find that

$\overset{+}{q}\, p_0 = \frac{k-i}{l}\, p_0$, and $\bar{q}\, p_0 = \frac{\bar{k}-\bar{i}}{l}\, p_0$, and $\overset{+}{p}\, p_0 = \frac{h-\bar{i}}{l}\, p_0$, and $\bar{p}\, p_0 = \frac{\bar{h}-i}{l}\, p_0$.

Our general formulae then become for pyramidal faces

$$\frac{\sin\phi\cdot\tan\rho}{\pm\sin 60^\circ} = \pm q p_0 = \frac{(\pm k)-(\pm i)}{l}\, p_0$$

$$\frac{\sin(60^\circ-\phi)\cdot\tan\rho}{\pm\sin 60^\circ} = \pm p p_0 = \frac{(\pm h)-(\mp i)}{l}\, p_0$$

and prisms

$$\frac{\dfrac{\sin(60^\circ-\varphi)}{\pm\sin 60^\circ}}{\dfrac{\sin\varphi}{\mp\sin 60^\circ}} = \frac{\pm p}{\mp q} = \frac{(\pm h)-(\mp i)}{(\mp k)-(\mp i)}.$$

The prism $11\bar{2}0$ is apparently an anomalous case for the values of $p$ and $q$ are 1 and 0, but where either $p$ or $q$ is zero the other Goldschmidt co-ordinate for a pyramidal face is $(3/2)\ h\cdot\ p_0/l$ and in the case of this prism the co-ordinate 1/0 must be looked upon as $(3/2)h/0$ from which the indices $11\bar{2}0$ can be readily deduced.

To illustrate the change involved, the mathematical calculations for a single face of each of the following forms on beryl $(10\bar{1}1)$, $(11\bar{2}2)$, $(11\bar{2}1)$ $(21\bar{3}1)$, $(10\bar{1}0)$ and $(21\bar{3}0)$ are given in the following table, using the values of $\varphi$ and $\rho$ that correspond to the positions of these forms as determined by the Koksharov axial ratios.

In the column devoted to the angle $\varphi$ the angle $V'$ is given. $V'$ is the angle measured from the zero position of the projection while $\varphi$ is the angle obtained by subtracting an integral multiple of 60° from $V'$. With this change in the magnitude of angle $\varphi$, and with $pp_0$ always greater than $qp_0$ as given in the formulae above, the position of $pp_0$ and $qp_0$ in the calculation becomes interchangeable.

| Bravais Symbol | $V'$<br>$\varphi$ | $\rho$ | log sin $60°-\varphi$<br>log tan $\rho$<br>log sin $\varphi$ | log $pp_0$<br>log $qp_0$ | $pp_0=\frac{h-i}{l}p_0$<br>$qp_0=\frac{k-i}{l}p_0$ | $p_0$<br>$p_0$ | $c=\frac{3}{2}p_0$ |
|---|---|---|---|---|---|---|---|
| $1\bar{1}01$ | 150°00′<br>30°00′ | 29°57′ | 969897<br>976056<br>969897 | 952200<br>952200 | +.33264<br>−.33264 | .33264<br>.33264 | .4989<br>.4989 |
| $\bar{1}2\bar{1}2$ | 0°00′<br>0°00′ | 26°31′ | 943753<br>969805<br>$\overline{\infty}$ | 969805<br>$\overline{\infty}$ | +.49895<br>.0000 | .33263 | .4989 |
| $\bar{1}\bar{1}21$ | 240°00′<br>0°00′ | 44°56′ | 993753<br>999899<br>$\overline{\infty}$ | 999899<br>$\overline{\infty}$ | +.99761<br>.0000 | .33254 | .4988 |
| $21\bar{3}1$ | 70°53.4′<br>10°53.4′ | 56°44′ | 987848<br>018307<br>927639 | 012402<br>052193 | −1.3305<br>+ .3326 | .33263<br>.3326 | .4989<br>.4989 |
| $21\bar{3}0$ | 70°53.4′<br>10°53.4′ | 90°00′ | 987848<br>—<br>927639 | $\log\frac{p}{q}$<br>060209 | $\frac{-p}{+q}=\frac{h-i}{k-i}$<br>−4.0003 | | |
| $1\bar{1}01$ | 150°00′<br>30°00′ | 90°00′ | 969847<br>—<br>969897 | $\log\frac{p}{q}$<br>000000 | $\frac{+p}{-q}=\frac{h-i}{k-i}$<br>−1.0000 | | |

The calculation gives no new determinations of $c:a$ but by using the angles that have been determined by others confirms the value obtained by Koksharov. For comparison the values are given below:

| | |
|---|---|
| Koksharov | $c=0.498855$ |
| Parsons (Arithmetic) | $0.498882$ |
| Goldschmidt | $0.8643=0.4989\sqrt{3}$ |

There has been much confusion in the treatment of hexagonal crystals by the two circle method because in either the $G_1$ or $G_2$ positions a multiplication or division by $\sqrt{3}$ or a multiple thereof is omitted. This is very evident when the Goldschmidt symbols are the same as those of other workers for in that case the value of $c$ has been multiplied by $\sqrt{3}$ to obtain the Goldschmidt $c$. Where Goldschmidt's $c$ is the same as that of other workers this is not so evident but it shows in his transformation formula

$$pq(G_2)=\frac{p-2q}{3}\cdot\frac{p-q}{3}\,(G_1)$$

which when multiplied by $\sqrt{3}$ becomes

$$p\sqrt{3}\cdot q\sqrt{3}(G_2)=\frac{p-2q}{\sqrt{3}}\cdot\frac{p-q}{\sqrt{3}}\,(G_1).$$

While the mathematical calculation of the crystallographic constants in the hexagonal system is quite simple, the theory underlying the equation for a plane in this system in terms of its intercepts, in terms of the co-ordinates for the line which is perpendicular to the plane, and in terms of its directional cosines, is decidedly complex. It is extremely easy to become confused as is illustrated by a tabulation of the values of $c/a$ as given by Goldschmidt in his Winkeltabellen and by Dana in the sixth edition of his System of Mineralogy, as shown in the table below where a single example is given for each type of difference.

It thus becomes evident that a complete revision of the hexagonal system is necessary for a ready interpretation of two-circle measurements, for there is a lack of agreement in the axial ratio or the symbols or both in every hexagonal mineral.

In spite of the confusion that has arisen from the two orientations $G_1$ and $G_2$ the fact remains that in his $G_1$ position Goldschmidt discovered the simplest method, although on an incorrect assumption, of determining graphically the Bravais indices of any face in the crystal after the unit pyramid $10\bar{1}1$ had been selected. In his $G_2$ position he had the simplest way of determining graphically $p_0$ and $c$. Unfortunately after finding that in every other system his co-ordinates could readily be converted into $a:b:c$ and $hkl$ he could not believe that when he had the indices determined by others his ratio of $c:a$ was incorrect and that when he accepted the standard ratio of $c:a$ his indices were wrong.

| | Dana | | Goldschmidt | |
|---|---|---|---|---|
| Bery | $\frac{c}{a}\times\sqrt{3}$ | = | $\frac{c}{a}\,G_1$ | $10\bar{1}0$ Dana $= 10\bar{1}0$ Goldschmidt |
| Microsommite | $\frac{c}{a}\times 2\sqrt{3}$ | = | $\frac{c}{a}\,G_1$ | $10\bar{1}0$ Dana $= 10\bar{1}0$ Goldschmidt |
| Breithauptite | $\frac{c}{a}\times\frac{2}{3}\sqrt{3}$ | = | $\frac{c}{a}\,G_1$ | $10\bar{1}0$ Dana $= 10\bar{1}0$ Goldschmidt |
| Calcite | $\frac{c}{a}$ | = | $\frac{c}{a}\,G_2$ | $10\bar{1}0$ Dana $= 11\bar{2}0$ Goldschmidt |
| Dioptase | $\frac{c}{a}\times 2$ | = | $\frac{c}{a}\,G_2$ | $10\bar{1}0$ Dana $= 11\bar{2}0$ Goldschmidt |
| Millerite | $\frac{c}{a}\times 3$ | = | $\frac{c}{a}\,G_2$ | $10\bar{1}0$ Dana $= 11\bar{2}0$ Goldschmidt |
| Covellite | $\frac{c}{a}\times 1.5$ | = | $\frac{c}{a}\,G_1$* | $10\bar{1}0$ Dana $= 11\bar{2}0$ Goldschmidt |

* Should be $G_2$.

Largely on account of the confusion caused by the $G_1$ and $G_2$ positions there has been considerable opposition on the part of some able crystallographers to the two-circle method. It is hoped that this paper may help to lessen this opposition, and serve as a preliminary to a complete revision of the angle tables for hexagonal minerals.

After this paper had been sent in for publication a much simpler method of calculating indices and axial ratios was found. After selecting the first order unit pyramid, making $\varphi$ not greater than 30° with $h>k>i$, then

$$\cos\varphi \cdot \tan\rho = \frac{h}{l} \cdot \frac{c}{a}$$

$$\cos(60° - \varphi) \cdot \tan\rho = \frac{k}{l} \cdot \frac{c}{a}$$

$$\cos(60° + \varphi) \cdot \tan\rho = \frac{i}{l} \cdot \frac{c}{a}$$

and for prisms

$$\cos\varphi : \cos(60° - \varphi) : \cos(60° + \varphi) = h : k : i.$$

This will be taken up in greater detail in a later paper.

# ON THE CRYSTALLOGRAPHY OF AXINITE AND THE NORMAL SETTING OF TRICLINIC CRYSTALS

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## Contents

Present Status of the Problem of Choosing Morphological Elements . . . . . 588
Course of the Present Study . . . . . 591
Several Steps in Choosing Normal Triclinic Elements . . . . . 592
  Determination of the Specific Lattice . . . . . 592
  Choice of the Representative Lattice Cell . . . . . 593
  Orientation of the Representative Lattice Cell . . . . . 593
Determination of Normal Elements from the External Geometry . . . . . 597
Determination of Normal Elements from *X*-Ray Measurements . . . . . 599
Relation of the New Lattice Elements to those of Gossner & Reichel . . . . . 602
Determination of the Optical Elements . . . . . 603
Definitive Presentation of the Crystallography of Axinite . . . . . 605
Some of the Existing Settings of Axinite and the Underlying Principles . . . . . 605
  Neumann (1825) . . . . . 605
  Lévy (1838)—Des Cloizeaux (1862) . . . . . 609
  Miller (1852) . . . . . 609
  Vom Rath (1866) . . . . . 610
  Schrauf (1870) . . . . . 611
  Goldschmidt (1886; 1897–1913) . . . . . 612
  Dana (1892) . . . . . 613
  Friedel (1926) . . . . . 613
Propriety of the Normal Setting of Triclinic Crystals . . . . . 615
Summary . . . . . 616
Acknowledgments . . . . . 617
References . . . . . 618
Explanation of the Figures . . . . . 618
Appendix: Transformation of Co-ordinates (J. D. H. Donnay) . . . . . 621

## Present Status of the Problem of Choosing Morphological Elements

The problem of choosing morphological crystallographic elements reaches full generality in the triclinic system, in which the mutual intersections of any three non-tautozonal crystal planes may be taken as axes of reference with the intercepts of any crystal plane cutting all the axes to define the parameters. If the indices of the observed planes are to be small numbers only a moderate number of morphological lattices come under consideration; but since a triclinic lattice may be defined by any one of numerous cells, and any triclinic cell can be oriented in twenty-four different ways, the number of sets of geometrical elements that can be chosen for any one triclinic species is still very considerable.

Is there a single solution to the problem of choosing triclinic elements in a given case, a solution which can justly be claimed as the correct one?

The question is of fundamental theoretical interest; and anyone who has attempted to correlate the crystallographic work on a much studied triclinic species will appreciate its practical importance.

Many serious studies have been directed toward finding the "correct" elements from purely morphological data. The more important principles that have been used are the following: the Principle of Simplest Cleavages,[1] which claims a closed cleavage form as the true primitive form, and cleavage planes in general as fundamental (simplest) lattice planes; the Principle of Simplest Indices,[2] according to which the proper elements are those resulting in the simplest face-symbols; the Law of Bravais,[3] by which elements are properly chosen when the relative importance of the observed crystal planes corresponds best with their respective reticular densities in the inferred Bravais lattice; the Law of Complication[4] and other number rules,[5] by which the principal crystal planes are determined and indexed so that the symbol series in the main zones approach most closely the particular number series believed to represent normal zonal development; the Principle of Highest Pseudo-Symmetry,[6] by which elements are chosen to exhibit the highest apparent or presumed pseudo-symmetry; and the Principle of Homeomorphism or morphological analogy,[7] according to which elements are chosen so as to bring out geometrical similarities between species believed to be more or less closely related.

None of these procedures has brought a satisfying general solution of the problem of selecting crystallographic elements; and the reason is that the principles on which they depend are not laws but hypothetical principles based on empirical generalizations which are only more or less true. Proceeding deductively from an adopted principle, such as the Principle of Simplest Indices or the Law of Bravais, a unique solution can always be reached, albeit indirectly and laboriously; but when the unique solutions from different postulates sometimes agree and sometimes differ, and the result of rigorous $x$-ray analysis gives still another solution which is entirely acceptable, it becomes increasingly clear that none of the morphological principles at present in use leads consistently to geometrical elements which can fairly be claimed as correct.

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[1] This principle originated in Haüy's conception of crystal structure. It is also accordant with the Law of Bravais, since cleavage planes are commonly lattice planes with the greatest spacings and, therefore, the highest reticular densities.

[2] This is the most widely used criterion; it has been particularly emphasized in recent years by Ungemach (1923) and Barker (1930).

[3] Logically developed and applied to a large number of species by Friedel (1904).

[4] Developed by Victor Goldschmidt (1897) and applied by him and many of his pupils to numerous species. The law is connected with Goldschmidt's theory of the development of crystal faces normal to principal crystal forces and their resultants, believed to reside in the crystal particle. In effect, the Law of Complication is an expression of the Law of Bravais in the special case a simple cubic lattice.

[5] Other number rules are the "Zielreihen" of Haag (1913) and the "Séries" of Ungemach (1935).

[6] Fundamental in the ideas of Fedorov and Barker, much used by Schrauf and Tschermak, and generally more or less recognized. Closely related to the Principle of Highest Pseudo-Symmetry is what may be called the Principle of Simplest Twinning Planes of Wallerant (1899); the Principle of Least Anorthism, which demands sub-rectangular axes in preference to axes more inclined; and the Sub-Cubic Rule, by which one chooses a parametral plane that slopes like the cubic octahedron in preference to one which is inclined much more or much less steeply to the vertical axis.

[7] Successfully used by the systematists, Dana and Hintze, but sometimes carried to extremes by Groth and others.

Since the analysis of crystal structures by means of $x$-rays has provided the means of directly determining the unique physical lattice, and this lattice always proves to be either geometrically similar to the well-chosen morphological lattice, or simply related to it, and in most cases eminently suitable for morphological purposes, it appears that morphological crystallographers have, in effect, been striving to find the physical lattice, with more or less success but never with certainty. It is not surprising that the empirical principles have proved uncertain; it is rather a matter of wonder that morphologists have in so many cases been led to adopt the lattice which has subsequently proved to be geometrically similar to the translation lattice of the crystal structure.

At this stage in the development of crystallography two courses are open: either we decide that $x$-ray analysis is bringing the solution of a problem which cannot be solved satisfactorily from morphological data; or, realizing that the physical lattices of only a small proportion of the known crystallized substances have been determined, we may approach the problem afresh by studying the relations of crystal forms to known structural lattices, thus learning to recognize these relations and to infer the structural lattice in other cases by choosing elements which most nearly result in similar relations. In this way the old problem of choosing geometrical elements is redefined as the problem of finding the geometrical equivalent of the structural lattice from the external geometry of the crystal; and instead of speaking of "correct elements," a vague phrase which has hitherto meant "elements which agree best with a preferred hypothetical principle," we shall consider "normal elements," meaning thereby unique geometrical elements which correspond to a cell of the structural lattice, selected and oriented according to widely accepted conventions. The "normal setting" is thus the setting which gives normal elements. These terms will be more sharply defined later, when the conventions involved have been severally stated.

The suggested course offers considerable promise of success in all but two situations. If the crystals have very few forms, or if they are very imperfectly developed, it may be impossible to discern the structural lattice or indeed any crystallographic lattice whatever. Again, if the crystal forms show the influence of two or more related lattices it may not be possible to select the structural lattice; but in such cases, which may properly be regarded as exceptions requiring special study, there may also be valid reasons for departing from the structural lattice for morphological description.[8] Experience with a fair number of crystallized minerals in the triclinic, monoclinic and orthorhombic systems indicates that, with proper criteria, it will be possible in most cases except those mentioned above, to discern the structural lattice, usually by simple inspection of the gnomonic projection of the known forms.

Before attempting to formulate the criteria which promise to solve the old problem of choosing crystallographic elements, it will be necessary to examine a sufficient number of special cases. In the present paper one example is studied with due consideration of the many variables which must be taken into account in the general case of the triclinic system. The course of such an examination having been established, other cases can be rapidly treated; and eventually, if the investigation is successful, it will be possible to formulate a simple general procedure for selecting normal elements from morphological data.

## Course of the Present Study

As an example of the most general case, axinite has been chosen, since it is triclinic, notably oblique and somewhat variable in habit, and free from obvious pseudo-symmetry and twinning which might prejudice the choice of morphological elements. Axinite appears the more suitable for the present purpose since it has been oriented in many different ways according to the particular principles preferred by the several responsible authors. Furthermore, the only published determination of the structural lattice gives yet another setting. But this determination is manifestly faulty; and therefore, apart from the theoretical problem in hand, a redetermination is desirable.

A well-developed crystal of axinite was sketched, measured on the two-circle goniometer and projected in gnomonic projection. Using criteria which in previously studied cases had led to the structural lattice, and a few well-known and generally accepted conventions governing the choice and setting of the representative lattice cell, unique geometrical elements were obtained by inspection and direct measurement of the gnomonic projection. These elements, which fulfil all the reasonable requirements of a good morphological setting, were found to differ in some respect from all those previously proposed.

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[8] See Ungemach (1935, p. 198) on calcite and other cases of multiple periods.

The same crystal was then used for a rigorous determination of the structure lattice with the Weissenberg *x*-ray goniometer, by means of which the necessary six lattice elements were found directly, without reliance on the known geometry. Employing the above-used conventions to select and orient the representative cell in the determined structural lattice, unique absolute elements were obtained. These elements, which differ from the published structural elements, were found to be proportional to the elements determined from the external geometry within narrow limits of experimental error. This agreement showed that in the chosen example of the most general case it was possible to infer the proportional elements of the structure lattice from the relations of the external crystal planes, and that, therefore, the provisional criteria used for this purpose were so far adequate.

From the determined structural elements and the known composition and specific gravity of axinite the atomic content of the unit cell was obtained. Using the same crystal, a redetermination of the optical orientation in relation to the new setting was also made. Recognizing the propriety of the new setting, Professor Charles Palache contributed a definitive presentation of the crystallography of axinite, one which will, it is believed, commend itself to those who look forward to a closer correlation of the results of morphological and structural investigations.

Finally, the existing orientations of axinite are reviewed and related to the new orientation by the appropriate transformation determinants. This correlation has practical value; and the review is of interest in affording a brief history of the development of ideas on the choice of geometrical elements.

## SEVERAL STEPS IN CHOOSING NORMAL TRICLINIC ELEMENTS

The problem of choosing crystallographic elements, morphologically or röntgenographically, resolves into three parts: (1) determination of the specific lattice; (2) choice of the representative lattice cell; (3) choice of orientation of the representative lattice cell. Thus resolved, the full problem with its many variables is easily envisaged.

*Determination of the Specific Lattice.* By specific lattice we mean the system of lattice points established by successive identity points in the crystal structure. The specific direct lattice is completely defined by any three non-coplanar identity periods in the structure of the crystal, together with the three angles made by the respective lattice rows. Similarly, the specific reciprocal lattice is defined by the reciprocals of the spacings of any three sets of non-tautozonal planes in the direct lattice, together with the three angles made by the respective normals to the three sets of lattice planes. Both in morphological and structural practice it is convenient to work with the reciprocal lattice and derive the direct lattice by calculation.

The specific reciprocal lattice is determined directly by $x$-ray analysis; the morphological problem centers on finding the geometrically similar lattice from the relations of the observed crystal planes. The problem is solved if we can recognize the points of the first layer of the reciprocal lattice in the gnomonic projection of the known forms. This, I believe, can usually be done; but since we are proceeding inductively, it will be better to defer the necessary argument and details until later.

*Choice of the Representative Lattice Cell.* Out of the unlimited number of lattice cells which may be used to define a given space lattice, structural crystallographers have agreed to use the smallest cell with the highest symmetry of the lattice. This entirely natural and proper convention should be equally binding in morphological crystallography. In the triclinic system every simple cell has the full symmetry of the lattice; and since all simple cells have the same volume, the "smallest cell" is understood to mean the cell whose edge-lengths are the three shortest non-coplanar lattice periods, and whose axial planes are, consequently, the three non-tautozonal lattice planes with the greatest spacings. Usually this unique cell can be found immediately by inspecting a construction of the direct or reciprocal lattice; its correctness can always be tested by showing that all the ten diagonals of the direct lattice cell are longer than its edges, or that all the ten diagonal planes have smaller spacings than the axial planes.

In the gnomonic projection in which the first layer reciprocal lattice points have been distinguished and missing points in the central region restored, the desired lattice cell is simply obtained by finding the three non-tautozonal first-layer points which are nearest the center of the projection. Take the point nearest center as an axial plane, provisionally (001); name the others provisionally (011), (101). The remaining axial planes (010), (100), and all the indices are thus provisionally determined, and the chosen cell is the cell whose axial planes have the three greatest non-tautozonal spacings in the direct lattice since the respective reciprocal lattice points are the three non-tautozonal points nearest the origin.

*Orientation of the Representative Lattice Cell.* To the structural crystallographer any one orientation of a determined triclinic lattice cell will serve as well as any other. The morphological crystallographer, on the other hand, is much concerned with the orientation of a crystal with respect to fixed space directions; and in this matter it is desirable that the structural worker consider the simple and reasonable requirements of good conventional morphological orientation.

As already stated, there are twenty-four possible orientations of a given triclinic cell. This number is readily verified: with either end of any of the three axes directed vertically upward (six possibilities) either end of either of the two remaining axes may be directed toward the observer in the vertical fore-and-aft plane (four possibilities), giving twenty-four orientations in all. If we agree to use right-handed axial systems, now in universal use, the twenty-four orientations give a like number of sets of unlike elements; if we admit left-handed axial systems, the possible number of sets of unlike elements which may be used to describe a triclinic lattice cell is raised to forty-eight.

Excluding left-handed axial systems, a unique good conventional morphological orientation of a triclinic lattice cell is reached in three steps: 1. Select the appropriate vertical axis without fixing its sense; when this has been done eight settings are possible, four with one end of the vertical axis directed upward, and four in the inverted position. 2. Let the base slope to the front and the right ($\phi_{001}$ between 0° and 90°; $\alpha$ and $\beta$ both obtuse), a condition which admits two of the eight available settings. 3. Of these two positions take the one in which the athwart axis $b[010]$ is longer than the fore-and-aft axis $a[100]$. These rules express generally accepted conventions of long standing, conventions designed to place a triclinic crystal in a favorable position as seen from the usual viewpoint, in which the eye is raised about 10° above the crystal centre and moved about 20° to the right of the vertical plane containing the fore-and-aft axis.

The judicious selection of the vertical axis is of prime importance; and if this axis is properly chosen at the very outset of a morphological or röntgenographic study the final desired orientation is quickly reached. The vertical axis is properly selected from a consideration of the normal crystal habit. If a crystal species is habitually acicular or columnar, the axis of the acicular or columnar zone is almost certainly an edge of the properly chosen lattice cell; and most morphologists will set this axis vertical for the sake of appearance alone. But aside from the matter of appearance, it is highly desirable for practical reasons that the axis of habitual morphological elongation be taken as the vertical axis, since this axis is the most convenient, sometimes the only practical axis of adjustment on the Goldschmidt reflecting goniometer and the Weissenberg $x$-ray goniometer, instruments which have a great advantage in giving complete lattice determinations with one crystal adjustment.

In the case of crystals which are habitually elongated and tabular to a plane in the elongated zone, morphologists are less consistent in setting the edge of the elongated zone vertical. But here the practical consideration mentioned above is equally valid and it is equally desirable that the edge of an elongated table be set upright.[9]

Crystals which are tabular without pronounced elongation are likely to have pseudo-dimetric lattices, clino-quadratic or clino-hexagonal, to use Schrauf's appropriate terms. Such lattices are properly set with the axis of dimetric pseudo-symmetry vertical, the plane of tabular development thus becoming the base.

Finally there is the possible but, in the triclinic system, infrequent case of habitual equant development, without consistent flattening or elongation. In such cases a study of all the available drawings of crystals of the species, assembled in Goldschmidt's *Atlas der Krystallformen*, might reveal a tendency toward elongation or flattening in certain directions, which would indicate the proper vertical axis. In a few cases, which might be expected among lattices of pseudo-cubic type, the crystal habit might give no indication of the proper vertical axis; in such cases one of the edges of the lattice cell, preferably the shortest, must be arbitrarily chosen as the vertical axis. Once this has been done, it would be frivolous for another worker to depart from this choice on the basis of one or two crystals which showed fortuitous departure from equant habit.

Once the vertical axis has been determined the only difficulty attending the unique orientation of a triclinic cell has been overcome. The two remaining rules can be immediately applied if the gnomonic projection of the external planes or the reciprocal lattice construction of the internal planes has been made on a plane normal to the adopted vertical axis. Either projection is simply turned about the vertical axis until the point (001) falls into the first quadrant ($\phi_{001}$ between 0° and 90°) when a vertical axial plane lies fore-and-aft. The base then slopes to the front and to the right where it is visible from the normal viewpoint. This rule is a logical extension of the inflexible rule in the monoclinic system which requires the base to slope to the front. If now the athwart axis (the macrodiagonal) is longer than the fore-and-aft axis (the brachydiagonal), and therefore the corresponding reciprocal lattice periods are in the converse relation, the desired orientation has been found. If not, the projection is inverted and viewed through the paper, and again turned about the vertical axis until the pole of the base lies in the first quadrant; then the macrodiagonal and brachydiagonal are necessarily in their proper relation and the required orientation has been attained. The macrobrachy rule, borrowed from the orthorhombic system, originates in the fact than an orthorhombic prism presents a more favorable aspect when viewed in the general direction of the shorter diagonal.

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[9] Ungemach, in particular, has frequently departed from the rule of setting the axis of columnar or elongated tabular development vertical, often setting such an axis fore-and-aft. The only possible advantage of such a position is that an entire termination can be seen from the usual viewpoint of an inclined drawing. But this is surely unimportant as against the advantage of obtaining a projection in normal position after mounting and measuring a crystal, known or unknown, in the usual manner. In the conventional setting a view of an entire termination is always given by a plan, the simplest and clearest of drawings.

Morphological elongation commonly takes place along the shortest lattice period, while habitual flattening, often associated with cleavage, usually follows the greatest lattice spacing, therefore transversely to the longest lattice period. Consequently the conventional orientation of habitually elongated crystals usually results in the shortest cell-edge becoming the vertical axis with the longest edge as the athwart axis; if the elongation is associated with tabular development and cleavage, these will almost certainly become side-pinacoidal. In the case of pseudodimetric crystals which are tabular to the plane containing the quasi-equivalent axes, the conventional setting places the longest cell-edge vertical.

Although the above rules are severally well recognized, they have not often been applied together to determine the desirable unique orientation of a triclinic lattice cell. One reason for this is probably the fact that although the rules are singly designed to place a crystal in a favorable position, some triclinic crystals of unusual or even typical habit may seem to present a better appearance in some other position. Since a good unique orientation is the main object, it is better in such cases not to depart from the conventional orientation but to shift the viewpoint, as is commonly done in the case of monoclinic crystals tabular to the plane of symmetry.

In review, we see that the core of the problem of finding normal triclinic elements from geometrical data may be reduced to the problem of distinguishing the first-layer points of the reciprocal structure lattice in the gnomonic projection of the external crystal planes. The proper vertical axis is chosen from a consideration of the normal crystal habit. The remaining variables are fixed by accepted rules, to which I have purposely added nothing beyond some elucidation which may serve to emphasize their validity. In the matter of the conventional orientation of a triclinic cell the recommendations given are in general agreement with those made by Donnay and Mélon (1933, p. 241) and Donnay, Tunell & Barth (1934, p. 445).

Having discussed the considerations which govern the reasoned choice of unique triclinic elements, we may proceed rapidly to their application to the chosen case of axinite.

## DETERMINATION OF NORMAL ELEMENTS FROM THE EXTERNAL GEOMETRY

All the observations in this paper were made on a single well-developed crystal of axinite detached from a specimen from near Easton, Pennsylvania, probably the same locality as "near Bethlehem, Pennsylvania," which yielded the axinite described by Frazier (1882). The crystal is 1.3 mm. in greatest dimension, and has a light-clove color; it is bounded by twenty-one faces, all but two of which give good reflections. One zone stands out prominently as the main zone, by virtue of the size and number of its faces; the axis of this zone was therefore taken provisionally as the vertical axis on the assumption, later proved, that it is an edge of the smallest cell of the structure lattice. The crystal was sketched, measured on the two-circle goniometer, and projected gnomonically on a radius of 10 cms. The plan of the crystal on the plane normal to the axis of the main zone and the corresponding projection are shown in figure 2; an inclined view of the crystal, with the lower termination symmetrically restored, is given in figure 4.

Elements believed to correspond to the normal setting of axinite were obtained from the gnomonic projection by means of the following considerations. If it is true that planes with simple indices in the proper lattice are more probable as crystal faces than planes with complex indices, then we will expect the reciprocal lattice representation of the forms of a triclinic crystal to be a system of points which can be referred to properly chosen reciprocal lattice axes $P\ Q\ R$ by co-ordinates $h\ k\ l$ which are simple multiples, 0, 1, 2 . . . , of properly chosen reciprocal lattice parameters, $p_0\ q_0\ r_0$. The degree of complication of the numbers $h\ k\ l$ will be determined by the complexity of the face development and by the relative lengths of the reciprocal lattice parameters; and the likelihood of occurrence of the numbers will be roughly proportional to their simplicity. Thus on the zero-layer of the reciprocal lattice $|h\ k\ 0|$ we shall expect the points (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, then (110), $(\bar{1}\bar{1}0)$, $(1\bar{1}0)$, $(\bar{1}10)$, then symbols containing 2, 3 . . . , in order of decreasing probability, according to the already mentioned limitations. On the first layer of the reciprocal lattice $|h\ k\ 1|$ we expect (001), (011), $(0\bar{1}1)$, (101), $(\bar{1}01)$, then symbols containing 2, 3 . . . . On the second layer of the reciprocal lattice $|h\ k\ 2|$, all points are already less probable since the third index is always 2; the points to be expected are those with the smallest indices, namely (012), $(0\bar{1}2)$, (102), $(\bar{1}02)$, etc. The third and higher reciprocal lattice layers will be still more weakly occupied.

Now the gnomonic projection is a two-dimensional representation of the reciprocal lattice. The direction lines to the vertical faces are parallel to lines joining the origin of the reciprocal lattice (000) to the corresponding reciprocal lattice points on the zero-layer. Let the plane of the gnomonic projection be the first layer of the reciprocal lattice; then the points in the plane of the gnomonic projection are either first-layer points ($h\ k\ 1$) in their true position in the reciprocal lattice, or projections of higher layer points ($h\ k\ n$), as given by the points of intersection of the plane of the gnomonic projection with lines joining the origin (000) to the corresponding reciprocal lattice points in the higher layers.

As already stated our problem is solved if we can distinguish the first-layer points from those on higher layers. The foregoing considerations lead us to expect the first layer will be occupied at all its points up to limits determined by the complexity of the face-development and the relative lengths of the lattice parameters. The first-layer points should therefore form a plane lattice in which the distances of the points in any row make an arithmetic series when measured from any point in that row. All points not at the nodes of this plane lattice are necessarily projections of reciprocal lattice points on higher layers, a point lying midway between two first-layer points representing a point on the second layer, a point lying one third of the way between two first-layer points representing a third-layer point, and so forth. Experience shows that there may be erratic omissions of reciprocal lattice points within the region of probability, and these constitute frequent and serious exceptions to the Law of Bravais; but we do not find systematic omissions in a simple triclinic lattice.

Since we have reason to believe that the first layer will be more fully represented by face-points than any higher layer, the first-layer points will be those points which fall on the plane lattice accommodating most of the points on the gnomonic projection without systematic omissions. Inspection of figure 2 shows that there is only one plane lattice that meets this requirement, namely that which has the points *c r e v y n Y x s* as nodal points. Only two terminal planes remain, *z* $\delta$, obviously second layer points. Any other choice of first layer lattice points results in systematic omissions which are inadmissible.

The first-layer points being fixed, the reciprocal lattice is fixed, and it only remains to select the cell whose axial planes are the three non-tautozonal planes with the greatest spacings, and set it in the conventional position. Taking the first-layer point which is nearest the centre of the projection, namely *c*, as an axial plane, provisionally (001), the next nearest, *r*, provisionally as (011), and the next nearest, *v*, provisionally as (101), the desired lattice cell is completely defined; *a*, *b*, *n*, receive the symbols (100), (010), (111), respectively, and all the remaining points are immediately indexed by inspection.

The chosen vertical axis proves to be the axis of the zone which is habitually the main zone of axinite and the one which has been chosen as the vertical zone by most previous workers. The base $c(001)$ slopes to the front and to the right ($\phi=89°55'$, calc.) and the reciprocal lattice period $cv$ ($p_0'=1.303$) is greater than the period $cr$ ($q_0'=0.999$), and consequently the direct period $b[010]$ is greater than the direct period $a[100]$, as required by the macro-brachy rule. The direct lattice cell is thus oriented in the one position out of twenty-four which satisfies the stated conventions; and the problem of finding normal elements for the given triclinic crystal appears to be solved, in less time than it takes to describe the procedure.

At this juncture it will be well to emphasize an important difference between the mode of discussion developed here and any procedure that accepts the Law of Bravais as strictly true. On the crystal used the faces $c(001)$, $a(100)$, and $a'(\bar{1}00)$ are small and they are habitually among the weaker planes of axinite. On a smaller crystal these planes might well have been absent; and anyone believing that axial planes, whose reticular densities are among the highest in any lattice are necessarily important crystal planes, would be forced to take planes other than $c$ and $a$ as axial planes. This is probably the reason why the French orientations take the large steep plane $r$ as the base, giving highly oblique lattices. With the present mode of discussion the final result would have been the same even if $c$ and $a$ were entirely absent; the remaining points are more than sufficient to establish the reciprocal lattice with complete certainty.

With the chosen elements the faces on the crystal are, on the zero layer: $b(010)$, $b'(0\bar{1}0)$, $a(100)$, $a'(\bar{1}00)$, $m(110)$, $m'(\bar{1}\bar{1}0)$, $M(1\bar{1}0)$, $M'(\bar{1}10)$, $l(1\bar{2}0)$, $l'(\bar{1}20)$; first layer: $r(011)$, $e(0\bar{1}1)$, $v(101)$, $y(\bar{1}01)$, $n(111)$, $Y(\bar{1}\bar{1}1)$, $x(\bar{1}11)$, $s(\bar{1}21)$; on the second layer: $z(012)$, $\delta(112)$.

By direct measurement on the gnomonic projection the normal projection elements of the axinite crystal were read off as follows:

$$p_0'=1.303,\ q_0'=0.999;\ x_0'=0.143,\ y_0'=0.000;\ \nu=102°35'.$$

By simple calculation these elements give the following polar elements, which are the geometrical elements of the chosen reciprocal lattice cell:

$$p_0:q_0:r_0=1.290:0.989:1;\ \lambda=90°00',\ \mu=82°07',\ \nu=102°35'$$

## DETERMINATION OF NORMAL ELEMENTS FROM X-RAY MEASUREMENTS

A precise determination of the structure lattice of axinite was made in the $x$-ray laboratory of the Geophysical Laboratory in Washington, with the instructive assistance of Dr. Barth, Dr. Tunell and Mr. Ksanda.

The instrument that was used is a Weissenberg $x$-ray goniometer built in the Fysisk Institutt of Norges Tekniske Høiskole at Trondheim, Norway, and improved by Tunell and Ksanda.[10] The effective radius of the camera is 35.0 mm., and the translation of the film carriage corresponding to 180° of rotation is 111.5 mm. The films were discussed by preparing two-fold enlargements with a precision pantograph made by Ksanda (1931), and projecting a sufficient number of reciprocal lattice layers by the construction of Schneider (1928), care being taken to plot lengths and angles in the proper sense. With these provisions, reciprocal lattice projections from Weissenberg photographs about a given axis are comparable with the corresponding gnomonic projection of the external planes, both in position with respect to the axis and meridian of reference, and in aspect; and the six absolute elements of the triclinic lattice are obtained by $x$-ray measurements alone, without reliance on the known external geometry of the crystal.

The photographs were made with Cu-K radiation which gave three to five layer-lines about the equator in rotation photographs and seven to eleven orders of diffractions from the more widely-spaced lattice planes on the Weissenberg photographs. The final values of the spacings of the axial planes were obtained by applying a small correction to allow for the crystal thickness, and placing most reliance on the higher order spots in which the $\alpha_1$ and $\alpha_2$ diffractions were clearly resolved and the effect of crystal thickness is at a minimum. Reciprocal axial angles were obtained by measuring the distances between rows of diffraction spots representing successive orders of diffraction from the axial planes, using a light box provided with a long glass cursor riding on a scale reading to a tenth of a millimeter by means of a vernier.

A rigorous although not highly accurate determination of a triclinic lattice is obtained from a rotation photograph about any zone edge and a first-layer Weissenberg photograph about the same axis. Better values are obtained if a zero-layer Weissenberg photograph is also made about the axis of reference; and with care this method gives excellent values,

[10] The improvements are the adaptation of the instrument to the equi-inclination method of Buerger (1934); and the addition of a graduated circle and two graduated arcs on the goniometer head, whereby a precision transfer of the head can be made from the $x$-ray goniometer to the Goldschmidt two-circle reflection goniometer suitably modified to receive the head in a precision bearing. Both the $x$-ray goniometer and the Goldschmidt reflection goniometer were fitted with verniers for reading the position of the head about its own axis on the new small circle permanently attached to the head. This circle lies in a plane perpendicular to the axis of the head. These additions permit a precision correlation of the external faces of a crystal with its structural (diffraction) planes, by the use of a direct beam spot made on each film when the external faces of the crystal are oriented in a defined manner. The method of carrying out this correlation between form and structure was worked out by Tunell and Ksanda and has been applied by them in their investigations of calaverite and krennerite" (*personal communication from Dr. George Tunell*).

as shown by the lattice determination of chalcanthite by Barth and Tunell (1933). But even with this method two of the lattice constants, namely the two reciprocal axial angles not included by planes in the zone of reference, are not very sharply defined since they are measured by the small horizontal shear of the first layer of the reciprocal lattice with respect to the zero-layer. The greatest accuracy is obtained by making additional zero-layer Weissenberg photographs about two further lattice rows; and subsequent calculations are greatly simplified if the three chosen axes of rotation are also the three non-coplanar lattice rows with the shortest periods. In this way each of the three reciprocal axial angles can be accurately measured on a zero-layer photograph, and three pairs of accurate values are obtained for the spacings of the axial planes. The less accurate values of the principal lattice periods obtained from rotation photographs about the three axes can then be neglected. This was done in the case of axinite with little difficulty, since the axis of the main zone of the crystal proved to correspond to one of the three shortest lattice periods, and both the remaining principal lattice rows were easily recognized as zone-edges on the crystal.

From the rotation photograph and the zero- and first-layer photographs about the axis of the main zone [001] the following values were obtained as the preliminary reciprocal elements of the simple translation cell with the shortest edges. Below are given for comparison the normal reciprocal elements previously obtained from the external geometry of the measured crystal.

$a^*=0.2225$, $b^*=0.1714$, $c^*=0.1733$; $\alpha^*=90°00'$, $\beta^*=80°04'$, $\gamma^*=102°33'$
$a^*:b^*:c^*=1.284:0.988:1$;
$p_0:q_0:r_0=1.290:0.989:1$; $\lambda=90\ 00$, $\mu=82\ 07$, $\nu=102\ 35$

Except for the difference of 2° between the angles $\beta^*$ and $\mu$, an insensitive angle when measured by reciprocal lattice shear, the agreement is good, and we have satisfying proof that the morphological discussion led to the smallest cell of the structure lattice. This result is gratifying, not on account of any difficulty in the morphological determination, but rather on account of the ease with which it was made, there being apparently no reasonable alternative to the adopted choice of elements.

The lattice constants obtained from rotation and Weissenberg photographs about the principal lattice axes are as follows:

| Axis of rotation | From rotation photographs | From Weissenberg photographs | | | |
|---|---|---|---|---|---|
| | | $d_{100}$ | $d_{010}$ | $d_{001}$ | |
| [100] | $a_0=7.1$ Å | — | 8.95 Å | 8.84 Å | $\alpha^*=89°55'$ |
| [010] | $b_0=9.1$ | 6.91 Å | — | 8.85 | $\beta^*=82\ 04$ |
| [001] | $c_0=9.0$ | 6.91 | 8.97 | — | $\gamma^*=102\ 33$ |
| Adopted mean spacings: | | 6.91 Å | 8.96 Å | 8.845 Å | |

The Weissenberg values give the following final structural lattice elements for axinite, with which are given for comparison Palache's geometrical elements subsequently deduced from numerous old and new measurements referred to the normal setting:

$a_0=7.151$ Å, $b_0=9.184$ Å, $c_0=8.935$ Å; $\alpha=91°52'$, $\beta=98°09'$, $\gamma=77°19'$
$a_0:b_0:c_0=0.7787:1:0.9729$; (Peacock)
$a:b:c=0.7789:1:0.9763$; $\alpha=91\ 51\frac{1}{2}$ $\beta=98\ 04$, $\gamma=77\ 14$
(Palache)

The excellent agreement confirms the belief of Barth and Tunell (1933) that careful $x$-ray goniometer measurements yield lattice elements comparable in accuracy with those obtained with the reflecting goniometer. With the additional Weissenberg photographs about two more axes the $x$-ray elements seem to be better than those obtained from the external planes of a single good crystal.

The volume of the unit cell is $V_0=566.8$ cub. Å; the molecular weight of the established formula of axinite, $HBAl_2Ca_2(Mn, Fe)Si_4O_{16}$, is 569.5, assuming that Mn and Fe are present in equal atomic proportions. With two formula weights in the unit cell we obtain a calculated density which lies near the upper end of the range of measured densities, as shown by comparison with the values taken from Dana (1892):

Density of axinite

| | |
|---|---|
| 3.271 | Haidinger |
| 3.294 | Rammelsberg |
| 3.299 | Genth |
| 3.306 | Genth |
| 3.316 | Peacock (from $x$-ray measurements) |
| 3.358 | Genth |

The unit cell of axinite therefore contains $H_2B_2Al_4Ca_4\,(Mn, Fe)_2Si_8O_{32}$, in which either Mn or Fe may preponderate and small proportions of Mg and other metals may enter.

## Relation of the New Lattice Elements to those of Gossner and Reichel

Gossner and Reichel (1932) made a determination of the structural lattice of axinite on a crystal from Bourg d'Oisans, combining measurements on a reflecting goniometer to determine an axial ratio, with $x$-ray measurements of the identity periods in a number of lattice rows whose angular relations were known from the external geometry. To show that their cell edges are the three shortest indentity periods in the lattice the authors list five further measured and calculated periods all of which are greater than their axial periods. The cell elements of Gossner and Reichel are related to ours as follows:

| Gossner & Reichel | Peacock |
|---|---|
| $a=T[100]=12.87$ Å | $T[110]=12.819$ Å (calc.) |
| $b=T[010]=7.15$ Å | $T[\bar{1}00]=7.151$ Å$=a_0$ |
| $c=T[001]=8.91$ Å | $T[001]=8.935$ Å$=c_0$ |
| $\alpha=[010]:[001]=82°26'$ | $[\bar{1}00]:[001]=81°51'=180°-\beta$ |
| $\beta=[001]:[100]=95\ 20$ | $[001]:[110]=95\ 52\frac{1}{2}$ (calc.) |
| $\gamma=[100]:[010]=135\ 35$ | $[110]:[\bar{1}00]=135\ 39\frac{1}{2}$ (calc.) |

Two of Gossner and Reichel's axial periods, $b$, $c$, are thus the shortest and second shortest periods in the axinite lattice while their third axial period, $a$, is the longer diagonal of our basal plane, as shown by the dotted cell in figure 3, and is the sixth shortest period in the lattice. It is difficult to understand this error since the roughest construction of Gossner and Reichel's lattice, which is essentially the same as ours as far as the lattice points are concerned, shows at once which are the shortest lattice periods. Gossner and Reichel also obtain a cell content with two formula weights which they write as follows: $2\{(SiO_4)_4Al_2B\ Ca_2MgH\}$; but this formula is not acceptable since it admits Mg as an essential constituent, whereas it is only an accessory, and neglects Mn and Fe which are always present in important amounts.

## DETERMINATION OF THE OPTICAL ELEMENTS

In view of the many existing crystallographic orientations of axinite, the possibility of real variations in the optical orientations in different axinites, and the chances of error in the published optical orientations, it seemed better to redetermine the optical orientation with reference to the new crystal setting rather than to transform an existing orientation. This was done on the Fedorov stage using the same crystal that was used for morphological and röntgenographic study. The orientation of the crystal was found by the satisfactory method of bringing a sufficient number of recognized crystal faces into the vertical fore-and-aft plane of the microscope and plotting the circle readings on the stereographic net. After bringing the three mutually rectangular planes of continuous extinction likewise into the vertical fore-and-aft plane of the microscope, plotting their poles, $X$, $Y$, $Z$, and determining the positions of the optic axes, the combined projection was turned into the adopted position giving the relations shown in figure 5. The diagram shows that the optical ellipsoid is strongly tilted in all directions to the crystallographic axes, with $X$, the acute bisectrix of the large optic axial angle, nearly normal to the crystal plane $x(\bar{1}11)$, as stated in the handbooks.

The optical orientation and the remaining measured optical elements are given in the following table, in which the two-circle angles of the principal ellipsoid axes, $X$, $Y$, $Z$, refer to the vertical crystallographic axis as pole and the vertical great circle through (010) as prime meridian. For comparison are given the optical elements of Des Cloizeaux (1862) and Berman, in Palache (1935), transformed to the new crystal setting.

### Optical Elements of Axinite

| Peacock: | (Na) | | $n$(Na) | | |
|---|---|---|---|---|---|
| | $\phi$ | $\rho$ | | | |
| $X$ (colorless) | −42° | 56° | 1.683 | ±0.002 | Negative |
| $Y$ (colorless) | 59 | 75 | 1.688 | | $2V=81°$ |
| $Z$ (colorless) | 168 | 39 | 1.692 | | $r<v$ weak |

| Des Cloizeaux: | | | $n$ (red) | $n$ (blue) | |
|---|---|---|---|---|---|
| | $\phi$ | $\rho$ | | | |
| $X$......... | −42° | 60° | 1.6720 | 1.6850 | Negative |
| $Y$......... | 54 | 81 | 1.6779 | 1.6918 | $2V=71°38'$ (red) |
| $Z$......... | 158 | 32 | 1.6810 | 1.6954 | 71 49 (blue) |

| Berman: | (Na) | | $n$(Na) | | |
|---|---|---|---|---|---|
| | $\phi$ | $\rho$ | | | |
| $X$ (yellow) | −24° | 55° | 1.684 | ±0.001 | Negative |
| $Y$ (yellow) | 79 | 72 | 1.692 | | $2V=74°$ |
| $Z$ (colorless) | 180 | 42 | 1.696 | | $r<v$ strong |

The three determinations agree sufficiently well to show that none contains gross errors; and the differences are not greater than might be expected from real variations in different materials combined with expected experimental errors. On the whole the writer's determination agrees more closely with that of Des Cloizeaux, which is to be expected if, as seems probable, both were made on ferro-axinite. Berman's measurements refer to a mangan-axinite from Franklin, N. J., in which a sensibly different orientation is probable.

The symbols and arrangement used in presenting the optical data are those which the writer has reached after studying the optics of several triclinic species and carefully considering the manner of presenting the results. In this arrangement the data are given in a logical order which is also approximately the order in which they are found, using accepted symbols: $XYZ$, the principal axes of the refractive index ellipsoid; the absorption colors of white light in these directions; $\phi\rho$, the co-ordinate angles precisely defining the orientation of ellipsoid axes with respect to the crystallographic axes, in this case for monochromatic light (Na); $n$(Na), the special lengths of the ellipsoid axes (refractive indices) for monochromatic light; and finally the dependent characters, optic sign and optic axial angle, and the nature of the dispersion of the optic axes.

A consistent optical statement in the monoclinic system has been used by the author (1936). In the orthorhombic system the corresponding statement is still simpler since the principal axes of the optical ellipsoid coincide with the crystallographic axes.

Many mineralogists use a single symbol to express a principle axis of the optical ellipsoid and its specific magnitude, the commonest symbols being $\alpha\beta\gamma$ for biaxial crystals and $\omega\epsilon$ for uniaxial crystals. Such compression of meaning may be justified when extreme economy of space is the object; but the writer finds it undesirable in principle and specially unfortunate in the triclinic system where $\alpha\beta\gamma$ mean axial angles in the intimately related field of geometrical crystallography. The suggested way of listing the refractive indices avoids this difficulty. If one wishes to write the refractive indices separately the logical symbols are $nX$, $nY$, $nZ$ for biaxial crystals, $nO$, $nE$ for uniaxial, crystals, $n$ for isotropic crystals, as suggested by Dr. W. T. Scaller in a personal communication.

## DEFINITIVE PRESENTATION OF THE CRYSTALLOGRAPHY OF AXINITE

The crystallography of axinite in the normal setting is here presented in a form which has been developed in the Harvard Mineralogical Laboratory, approved by a number of interested mineralogists in this country and abroad, and adopted in the preparation of crystallographic material for a projected volume of crystallographic angle-tables and the new edition of Dana's System of Mineralogy. The preparation of this statement is largely the work of Professor Charles Palache, who undertook the considerable labor of deriving the new geometrical elements, critically revising the form-list, and computing the co-ordinate and interfacial angles.

The statement aims at combining the data required by single-circle and two-circle crystallographers with those röntgenographic data that seem at the present time to have direct bearing on mineralogy as a branch of natural history. The symbolism and contractions are for the most part self-explanatory; those relating to the geometrical crystallography are explained in full in a paper by the writer (1934). The angles apply to the particular plane given by the Miller symbol in the form-list. The form-letters are, as far as possible, the classical letters, only those for {100}, {010}, {001}, {110}, $\{1\bar{1}0\}$, being changed to *a b c m M* respectively. For the uncertain forms letters are omitted as superfluous. The statement given is actually that planned for the projected Angle-Tables; in the System the list of calculated angles will of necessity be reduced to save space.

## SOME OF THE EXISTING SETTINGS OF AXINITE AND THE UNDERLYING PRINCIPLES

*Neumann (1825)*.[11] The first geometrically correct presentation of the morphology of axinite was given by Neumann (1825), soon after the appearance of his remarkable treatise (1823) proposing to use the gnomonic projection in crystallography and co-ordinates in this projection as face-symbols. In his axinite study, however, Neumann uses the stereographic projection—also a novelty in crystallography at that time—and Weiss

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[11] Haüy's determination of the primitive form of axinite contains errors which later workers have been unable to resolve.

### AXINITE[1]—$HBAl_2Ca_2 (Mn, Fe) Si_4O_{16}$

Triclinic; pinacoidal—$\bar{1}$

$a:b:c=0.7789:1:0.9763$; $\alpha=91°51\frac{1}{2}'$, $\beta=98°04'$, $\gamma=77°14'$[2]
$p_0:q_0:r_0=1.2845:0.9911:1$; $\lambda=89\ 55$ , $\mu=82\ 09$ , $\nu=102\ 38$
$p_0'=1.2973$, $q_0'=1.0010$; $x_0'=0.1418$, $y_0'=0.0016$

| Forms[3] | | $\phi$ | $\rho$ | $A$ | $B$ | $C$ |
|---|---|---|---|---|---|---|
| $c$ | 001 | 89°23′ | 8°04′ | 82°09′ | 89°55′ | 0°00′ |
| $b$ | 010 | 0 00 | 90 00 | 102 38 | 0 00 | 89 55 |
| $a$ | 100 | 102 38 | 90 00 | 0 00 | 102 38 | 82 09 |
| $\sigma$: | 130 | 24 58 | 90 00 | 77 40 | 24 58 | 86 31½ |
| $\gamma$ | 120 | 36 23 | 90 00 | 66 16 | 36 22 | 85 09 |
| $m$ | 110 | 60 28 | 90 00 | 42 10½ | 60 27½ | 82 56½ |
| $X$ | $2\bar{1}0$ | 121 46½ | 90 00 | 19 08½ | 121 46½ | 83 11½ |
| $I$ | $5\bar{4}0$ | 130 35 | 90 00 | 27 57 | 130 35 | 83 56½ |
| $M$ | $1\bar{1}0$ | 135 25½ | 90 00 | 32 47½ | 135 25½ | 84 24½ |
| $K$ | $9.\overline{11}.0$ | 139 58½ | 90 00 | 37 20½ | 139 58½ | 84 53½ |
| $\alpha$ | $3\bar{4}0$ | 141 58 | 90 00 | 39 20 | 141 58 | 85 06½ |
| $T$ | $11.\overline{16}.0$ | 143 57½ | 90 00 | 41 19½ | 143 57½ | 85 20 |
| $H$ | $2\bar{3}0$ | 144 39½ | 90 00 | 42 01½ | 144 39½ | 85 25 |
| $\beta$ | $3\bar{5}0$ | 147 01 | 90 00 | 44 23 | 147 01 | 85 41½ |
| $l$ | $1\bar{2}0$ | 151 01½ | 90 00 | 48 23½ | 151 01½ | 86 11 |
| $h$ | $1\bar{3}0$ | 158 56 | 90 00 | 56 18 | 158 56 | 87 11½ |
| $z$ | 012 | 15 46 | 27 33 | 88 33 | 63 34 | 26 21 |
| $j$ | 035 | 13 15 | 31 44½ | 89 40½ | 59 11½ | 30 43½ |
| $\phi$: | 034 | 10 40½ | 37 26½ | 91 11½ | 53 19 | 36 36 |
| $L$ | 045 | 10 01½ | 39 10½ | 91 39 | 51 32 | 38 23 |
| $r$ | 011 | 8 03 | 45 21½ | 93 15½ | 45 12½ | 44 42½ |
| $\pi$ | 021 | 4 03 | 63 32 | 97 40½ | 26 45 | 63 10 |
| $\phi$ | 031 | 2 42 | 71 36½ | 99 25½ | 18 35 | 71 20 |
| $\Lambda$ | 061 | 1 21 | 80 33 | 101 07½ | 9 32½ | 80 22½ |
| $e$ | $0\bar{1}1$ | 171 55½ | 45 16 | 75 27 | 134 42 | 44 47 |
| $\Delta$ | $0\bar{2}1$ | 175 56½ | 63 30 | 75 06½ | 153 12½ | 63 17½ |
| $Z$ | $0\bar{4}1$ | 177 58½ | 75 59 | 75 47 | 165 50 | 75 55 |
| $v$ | 101 | 101 20 | 55 08½ | 34 53 | 99 16½ | 47 16 |
| $\mu$ | 201 | 101 57 | 69 54 | 20 06½ | 101 12½ | 62 02½ |
| $R$ | 401 | 102 08 | 79 22 | 10 43 | 101 55 | 71 26 |
| $F$ | $\bar{1}04$ | −67 27½ | 10 42½ | 100 33 | 85 55 | 18 24 |
| $g$ | $\bar{1}03$ | −71 03 | 16 30 | 106 24 | 84 42½ | 24 15 |
| $\Pi$ | $\bar{2}05$ | −72 28½ | 20 55 | 110 50 | 83 49½ | 28 41½ |
| $f$ | $\bar{1}02$ | −73 43 | 27 06 | 117 02½ | 82 40 | 34 53½ |
| $y$ | $\bar{1}01$ | −75 45½ | 49 13½ | 139 12 | 79 15½ | 57 03 |
| $\iota$ | $\bar{2}01$ | −76 36½ | 67 51 | 157 50½ | 79 37 | 75 41½ |
| $\delta$ | 112 | 65 03½ | 40 30½ | 58 59½ | 74 06 | 33 15½ |
| $n$ | 111 | 62 51 | 57 41 | 49 26 | 67 24 | 50 32½ |
| $k$ | 221 | 61 45½ | 71 46 | 44 06 | 63 17½ | 64 40 |
| $\psi$ | $\bar{1}\bar{1}3$ | −130 17 | 20 10 | 102 00 | 102 53 | 26 51½ |
| $o$ | $\bar{1}\bar{1}2$ | −126 01 | 31 16 | 110 00½ | 107 46 | 38 06 |
| $Y$ | $\bar{1}\bar{1}1$ | −122 29 | 53 07 | 124 21½ | 115 26½ | 60 04 |
| $V$ | $1\bar{1}2$ | 129 35½ | 45 09 | 50 48½ | 116 52 | 39 16 |
| $x$ | $\bar{1}11$ | −41 09 | 59 39½ | 134 07½ | 49 28 | 65 04 |

AXINITE—$HBAl_2Ca_2(Mn, Fe)Si_4O_{16}$ (*Concluded*)

| Forms | | φ | ρ | A | B | C |
|---|---|---|---|---|---|---|
| ξ | 163 | 16 27 | 63 19½ | 86 35½ | 31 01 | 61 14 |
| τ | 183 | 12 20½ | 69 14 | 90 16½ | 24 01 | 67 38½ |
| ζ | $\bar{2}\bar{1}5$ | −103 09½ | 20 31 | 108 24 | 94 34½ | 28 26½ |
| ε | 132 | 29 39 | 57 26½ | 75 43½ | 42 54 | 53 40 |
| λ | $\bar{3}\bar{2}5$ | −110 19 | 33 22½ | 117 29½ | 101 00½ | 41 03 |
| Σ | $\bar{2}\bar{1}3$ | −101 30½ | 35 37½ | 122 06½ | 96 40 | 43 34 |
| *Q* | $\bar{5}87$ | −29 29 | 57 09 | 124 17½ | 43 00½ | 61 18½ |
| *d* | 121 | 39 18 | 65 46½ | 65 50½ | 45 07 | 60 46 |
| Ω | $\bar{4}14$ | −64 31½ | 51 14 | 139 28½ | 70 24½ | 58 33 |
| Θ | $\bar{3}23$ | −49 43 | 55 50 | 137 07½ | 57 39½ | 62 04½ |
| Φ | $\bar{4}54$ | −36 11 | 62 17½ | 131 47 | 44 23½ | 67 09½ |
| *W* | $\bar{2}32$ | −32 10½ | 64 39 | 129 33½ | 40 06 | 69 03 |
| *s* | $\bar{1}21$ | −26 10 | 68 34½ | 125 41 | 33 20 | 72 13½ |
| *i* | $\bar{1}31$ | −18 52½ | 73 57 | 120 08½ | 24 35 | 76 36½ |
| σ | $\bar{1}\bar{2}1$ | −146 47 | 64 01 | 108 25½ | 138 46 | 68 41 |
| *p*: | $\bar{7}\bar{3}5$ | −97 03½ | 58 40½ | 143 32½ | 96 11½ | 66 41½ |
| θ | 312 | 87 51 | 63 54½ | 29 43½ | 88 04 | 55 51 |
| *X*: | 322 | 74 12½ | 64 45 | 37 18 | 75 45 | 56 59½ |
| λ: | $\bar{3}\bar{1}2$ | −92 23½ | 60 22½ | 147 05½ | 92 04½ | 68 26½ |
| Γ | $\bar{3}22$ | −50 53½ | 66 10½ | 144 58 | 54 45½ | 72 28 |
| *t* | 231 | 47 39 | 74 33 | 56 25½ | 49 30½ | 68 36½ |
| ν | $\bar{2}11$ | −56 42 | 70 43½ | 152 02 | 58 47 | 77 28½ |
| *q* | $\bar{2}\bar{1}1$ | −100 14½ | 67 37½ | 148 25½ | 99 28 | 75 35 |
| ρ | $\bar{2}\bar{3}1$ | −135 31½ | 73 39½ | 120 29½ | 133 12½ | 79 27 |

*Structure cell:* Triclinic; $a_0=7.151$, $b_0=9.184$, $c_0=8.935$; $\alpha=91°52'$, $\beta=98°09'$, $\gamma=77°19'$; $a_0:b_0:c_0=0.7787:1:0.9729$. Contains: $H_2B_2Al_4Ca_4(Mn, Fe)_2Si_8O_{32}$.[4]

*Habit:* Oblique tabular $\{010\}$ or $\{011\}$, rarely $\{\bar{1}11\}$; rarely columnar [001]. Common forms: *b r M l s x a y; b M* often striated [001]; *r* often striated [010]. Also lamellar, massive, granular.

*Cleavage:* $\{100\}$ distinct; also $\{001\}$, $\{110\}$, $\{011\}$ interrupted; $\{010\}$, $\{\bar{1}01\}$ traces.[5]

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[1] Haüy (*Jour. Mines*, **5**, 264, 1799).

[2] Palache (1937), from previous measurements and new observations, in the orientation of Peacock (1937). The adopted setting differs from that of Dana (*System*, 1892) and Goldschmidt (*Winkeltabellen*, 1897; *Atlas*, 1, 1913).

*Transformations:* Dana to Palache—Peacock: $\bar{1}\bar{1}0/200/002$; Goldschmidt to P.—P.: $\bar{1}00/0\bar{1}0/001$.

[3] Goldschmidt (1913), Flink (*Ark. Kemi*, **6**, 111, 1917); Aminoff (*Ark. Kemi*, **7**, 45, 1919); Poitevin (*Amer. Min.*, **4**, 32, 1919; Buttgenbach (*Bull. Acad. Roy. Belge*, **10**, 141, 1924).

Uncertain: $\{210\}$, $\{14.1.0\}$, $\{21.\bar{1}.0\}$, $\{7\bar{2}0\}$, $\{9\bar{4}0\}$, $\{4\bar{3}0\}$, $\{970\}$, $\{12.13.0\}$, $\{10.\bar{1}\bar{1}.0\}$, $\{9.\bar{1}\bar{0}.0\}$, $\{15.\bar{1}\bar{7}.0\}$, $\{7\bar{8}0\}$, $\{4\bar{5}0\}$, $\{9.\bar{1}\bar{6}.0\}$, $\{18.\bar{1}\bar{7}.0\}$, $\{2\bar{9}0\}$, $\{1.\bar{1}\bar{3}.0\}$, $\{1.\bar{1}\bar{8}.0\}$, $\{1.\bar{2}\bar{6}.0\}$, $\{1.\bar{3}\bar{4}.0\}$, $\{058\}$, $\{056\}$, $\{091\}$, $\{0\bar{5}9\}$, $\{078\}$, $\{0.\bar{2}\bar{7}.28\}$, $\{\bar{2}03\}$, $\{\bar{3}01\}$, $\{\bar{2}\bar{2}1\}$, $\{13.46.\ 11\}$, $\{641\}$.

[4] Peacock (1937), on a crystal from near Easton, Northampton Co., Penn. The structure cell of Gossner & Reichel (*Centralb. Min.*, 1932, 225) defines nearly the same lattice, but its edges are not the three shortest identity periods in the lattice.

[5] Dana (1892).

symbols, which are the intercepts of the crystal planes on the direct axes.

Using a simple reflecting goniometer, provided with an auxiliary device which appears to have been a peep-sight, Neumann measured the following five interfacial angles on a typical crystal of axinite from the Dauphiny. These angles, which are astonishingly close to the corresponding calculated angles taken from Palache's new angle-table, were used as the basis of calculation.

| Neumann | Palache | Diff. |
|---|---|---|
| $vy=139°29'$ | $ay=139°12'$ | $3'$ |
| $ux=149\ 26$ | $Mx=149\ 28\frac{1}{2}$ | $2\frac{1}{2}$ |
| $xy=150\ 08$ $(29°52')$ | $xy\ =\ 29\ 47\frac{1}{2}$ | $4\frac{1}{2}$ |
| $vu=147\ 05$ $(32\ 55\ )$ | $aM=\ 32\ 47\frac{1}{2}$ | $7\frac{1}{2}$ |
| $vx=134\ 02$ | $ax=134\ 07\frac{1}{2}$ | $5\frac{1}{2}$ |

Although the existence of oblique axial systems was clearly recognized in Neumann's time, some crystallographers still followed Weiss in his belief that all form systems could be referred to rectangular axes with reasonable rational symbols. To demonstrate this in the case of axinite Neumann assumed that the angle $PM$ (89°55′ Neumann; $bc=89°55'$ Palache) is exactly a right-angle and denoted the sixteen known forms of axinite with rational but complicated symbols on the orthorhombic axes:

$$a:b:c=\sqrt{51}:\sqrt{49}:\sqrt{1}.$$

The axial planes and parametral plane of Neumann and the present writer are interrelated as follows:

| Neumann | | Peacock |
|---|---|---|
| $-(100)$ | = | $-(720)$ |
| $P(010)$ | = | $b(010)$ |
| $-(001)$ | = | $-(\bar{7}.\bar{2}.63)$ |
| $-(111)$ | = | $-(017)$ |

| Peacock | | Neumann |
|---|---|---|
| $a(100)$ | = | $v(9\bar{2}0)$ |
| $b(010)$ | = | $P(010)$ |
| $c(001)$ | = | $M(101)$ |
| $n(111)$ | = | $n(10.5.1)$ |

and the determinant[12] for transforming Neumann's symbol for any plane to the symbol which that plane receives in our lattice is:

Neumann to Peacock: $70\bar{7}/29\bar{2}/0.0.63$.

Neumann's symbols are, of course, intolerably complicated and his choice of lattice is entirely unacceptable; but this ingenious *tour de force* is of interest in showing the Principle of Least Anorthism, or Highest Pseudo-Symmetry, in its earliest and most uncompromising form. Even when tempered with some regard for simplicity of indices this principle has led to many crude settings. To-day one may rightly insist that a multiple lattice with high pseudo-symmetry should never be taken in preference to a simple lattice, unless the crystals habitually exhibit the pseudo-symmetry of the multiple lattice.[13]

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[12] Derived in the simple Fedorov manner, as described by Barker (1930), and written in Barker's convenient linear style. This and the following determinants give the strict plane to plane transformations, not just form to form.

*Lévy* (*1838*)—*Des Cloizeaux* (*1862*): Des Cloizeaux (1862) adopted the setting of Lévy whose numerous excellent drawings of axinite have established the familiar and most satisfactory aspect of the crystals. Des Cloizeaux took three of the most important (common and large) crystal faces as the faces of his primitive form, namely *p m t*,[14] which are respectively our *r*(011), *b*(010), $M'(\bar{1}10)$, his axial planes and parametral plane having the following symbols in our lattice:

| Des Cloizeaux | | Peacock |
|---|---|---|
| *h*′ (100) | = | *l*′ $(\bar{1}20)$ |
| *g*′ (010) | = | *a*′ $(\bar{1}00)$ |
| *p* (001) | = | *r* (011) |
| – (111) | = | – $(\bar{2}31)$ |

Des Cloizeaux to Peacock: $\bar{1}\bar{1}0/201/001$

Des Cloizeaux' vertical axis is thus the same as ours, but his elementary lattice cell is highly oblique and his parametral plane is not among the known forms of axinite. It is not surprising therefore that Des Cloizeaux' symbols are systematically more complicated than the simplest that can be found.

The practice of taking the most prominent planes in the vertical zone as "prisms" rather than as "pinacoids" has a sound basis in the higher symmetries when the lattices are appropriately centered; but in the triclinic system this procedure generally leads to a double (base-centered) cell and systematic complication of the indices. E. S. Dana (1892) often worked on this principle, as may be seen from his settings of rhodonite, babingtonite and aenigmatite, in each of which elements corresponding to those of the smallest cell of the structure lattice are obtained when Dana's unit "prisms" are taken as the vertical axial planes.

*Miller* (*1852*): Miller's writings are noteworthy for their brevity and elegance, admired and successfully emulated by Dana (1892). His presentation of the crystalllography of axinite is a model of clarity and condensation. Whether guided by the Principle of Simplest Indices, or simply by a sense of propriety, we cannot tell; but the fact is that Miller chose as his primitive parallelepiped the same cell that we have found from morphological and structural study, with the same edge set vertical. That our orientation of this cell about the vertical axis is different from Miller's is of no consequence in the present connection; that is merely a matter of convention which might well have been waived in the present case, were it not for the fact that Miller's indices could not in any case be retained unchanged since they refer to a left-handed axial system. Below are given the equivalent planes in Miller's lattice and in ours, and the transformation determinant, Miller's order of indices being retained.

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[13] In this connection see the author (1936).

[14] It will be remembered that the vertical faces of the "forme primitive" of the early French School are the vertical diagonal planes of the conventional lattice cell, and *vice versa;* furthermore Lévy's axes, like Miller's, read right—front—up, in the opposite order to that generally used today.

| Miller | | Peacock |
|---|---|---|
| *v* (100) | = | *a'* $(\bar{1}00)$ |
| *p* (010) | = | *b* (010) |
| *m* (001) | = | *c* (001) |
| *x* (111) | = | *x* $(\bar{1}11)$ |

Miller to Peacock: $\bar{1}00/010/001$

With Miller's satisfying presentation available, giving the simplest possible indices to the crystal planes then known and subsequently found and the most desirable aspect to the crystals, it is a matter of surprise and regret that the crystallography of axinite should have been later complicated by numerous re-orientations, the reasons for which now seem totally inadequate.

*Vom Rath* (*1866*): In his monographic study of the morphology of axinite—a fine example of the master's incomparable skill in crystal measurement and drawing—vom Rath (1866) described axinite crystals from many localities, using Quenstedt's linear projection and Weiss symbols in his geometrical treatment. After reviewing the previous orientations of axinite and discoursing on the wide range of choice of elements in the triclinic system, vom Rath indicates that one should reduce the choice by seeking a subrectangular axial system among the zone-edges made by the intersections of observed crystal planes. Vom Rath's choice, according to this limitation, is expressed as follows:

| Vom Rath | | Peacock |
|---|---|---|
| *s* (100) | = | *s* $(\bar{1}21)$ |
| *b* (010) | = | *v'* $(\bar{1}0\bar{1})$ |
| *c* (001) | = | *Y* $(\bar{1}\bar{1}1)$ |
| —(111) | = | $\iota$ $(\bar{2}01)$ |

Vom Rath to Peacock: $\bar{1}\bar{1}\bar{2}/20\bar{2}/1\bar{1}2$

While the guiding principle indicated by vom Rath is a useful one, it was poorly applied in the present case. Actually vom Rath's axes are on the whole more inclined than ours; and since they are defined by the intersections of planes with relatively complicated indices in the structure lattice, the tenor of vom Rath's face symbols is more complex than that of most of the previous and subsequent settings. This has been noticed by several later workers and vom Rath himself seems to have regretted his choice of elements as the work progressed; but by then he was too deeply involved in his elaborate calculations and drawings to undertake a change.

The infelicity of vom Rath's orientation is already apparent in the attitude of his drawings, of which twenty-eight complicated but clear examples are reproduced on a single plate measuring 11 by 14 inches. One is struck at once by the absence of a prominent vertical zone and the large development of zones whose axes are inclined to the crystal axes. Apart from the inelegance and practical inconvenience of a feeble vertical zone, such a condition points to a false choice of vertical axis, since the axial zones of a normally developed triclinic crystal are usually the strongest on the crystal, the strongest of all being best taken as the vertical zone to ensure that the vertical axis is an edge of the smallest cell of the structure lattice.

*Schrauf (1870)*: Schrauf's avowed morphological procedure was to choose as symmetrical a setting as possible, and at the same time bring out morphological analogies which seemed to exist between different species. In the case of axinite, after reviewing the eight existing orientations and stating that he would gladly refrain from proposing another setting, were it not for the fact that a better one was to be found, Schrauf proceeds to a new choice of elements which purports to give axinite a desirable pseudo-monoclinic aspect, to exhibit a morphological and optical analogy with sphene, and to result in a simplification of indices. In this attempt Schrauf is singularly unsuccessful. In his setting the forms of axinite are less markedly pseudo-monoclinic than they are in ours; the angles which he tabulates as comparable in axinite and sphene differ by 6° to 23° while the optical analogy is vague; and his indices, certainly simpler than the unhappy symbols of vom Rath, are notably more complicated than those of Miller, which he also gives for comparison. The correlation and transformation of Schrauf's symbols are given by the following:

| Schrauf | | Peacock |
|---|---|---|
| *a* (100) | = | *y′* $(10\bar{1})$ |
| *b* (010) | = | *v* (101) |
| *c* (001) | = | *b′* $(0\bar{1}0)$ |
| *u* (111) | = | *M* $(1\bar{1}0)$ |

Schrauf to Peacock: $110/00\bar{2}/\bar{1}10$

Schrauf's own transformation formulas relating his setting to those of Miller, Des Cloizeaux and vom Rath, are all in error in that the signs should be reversed throughout; and all later writers have repeated this error. This has far-reaching effects in Hintze, who used Schrauf's setting as the basis of his presentation and correlation. Schrauf's beautiful drawings representing fully developed crystals from several localities all lack prominent vertical edges; this mars the appearance of the figures and points to the poor choice of vertical axes.

On the ill-considered use of the principle of highest pseudo-symmetry we have spoken in this paper and elsewhere (author, 1936); even greater crudities have been committed in the name of morphological analogy or homeomorphism. Before the means were available for determining absolute lattice parameters it was reasonable to assume that isogeometrical crystals are related; and in many cases this presumption has been brilliantly confirmed by $x$-ray study, the species believed to be related proving to be isodimensional or isostructural.[15] Such confirmation of presumed structural similarity and systematic relationship has followed in cases of chemically similar species with similar naturally chosen lattices, usually accompanied with similarities of habit and cleavage. But when geometrical similarities have been forced by taking lattices which result in relatively complicated indices for one or both of the species, admitting gross differences in axial lengths and angles and differences of lattice symmetry, and ignoring important differences of cleavage, habit and chemical constitution, the imagined systematic relationship has found no confirmation in the absolute dimensions of the structure lattices and the arrangement of the cell contents. Frazier's setting of axinite (1882), intended to bring out geometrical and systematic similarity with the pseudo-orthorhombic monoclinic species datolite, is another case in point. Considerations of morphological analogy should be allowed to influence only the arbitrary factors in choosing elements, namely those which control the orientation of the properly chosen lattice cells; and such analogies can hardly be expected to have systematic significance except when accompanied by chemical and physical similarities.

*Goldschmidt (1886)*: In the *Index* (1886) Goldschmidt founded his setting of axinite on that of Miller, in which the symbol series approach normal complication series most closely. His position of the lattice cell, however, is different from Miller's and ours.

[15] *Isogeometrical* describes crystal species whose forms can be referred to like morphological lattices. *Isodimensional* (with like absolute lattice elements) may also be a useful term, as distinct from *isostructural* (with like structures), to describe the similarity between such species as rhodonite and babingtonite, which have like structural lattices, but can hardly be isostructural in view of their unlike chemical compositions. Isogeometrical, isodimensional and isostructural species are all *homeomorphous*.

| Goldschmidt (1886) | | Peacock |
|---|---|---|
| *M* (100) | = | *a′* (1̄00) |
| *m* (010) | = | *c* (001) |
| *c* (001) | = | *b* (010) |
| *x* (111) | = | *x* (1̄11) |

Goldschmidt (1886) to Peacock: 1̄00/001/010

Goldschmidt thus turned Miller's lattice cell so that Miller's vertical axis, which is the axis of the main zone, became the athwart axis and the weakest axial zone became the vertical zone. In thus resetting axinite Goldschmidt followed a peculiar principle which ignored tradition, appearance and convenience and aroused much opposition; this was to set the weakest axial zone of a crystal vertical, thus bringing as many as possible of the gnomonic face-poles into finite positions on the gnomonic projection where their serial relations could be most easily viewed and discussed.

In the *Winkeltabellen* (1897) Goldschmidt recognized the objection to many of his settings in the *Index* and reverted to classical orientations which he retained in the *Atlas* (1913–1924). In the case of axinite he again took Miller's lattice cell and set it in yet another position which agrees with ours when the crystal is turned 180° about the vertical axis.

| Goldschmidt (1897) | Peacock |
|---|---|
| *M* (100) | *a′* (1̄00) |
| *c* (010) | *b′* (01̄0) |
| *m* (001) | *c* (001) |
| *Y* (111) | *Y* (1̄1̄1) |

Goldschmidt (1897) to Peacock: 1̄00/01̄0/001

In transforming the elements Goldschmidt unfortunately gave values for the axial angles $\alpha$ and $\gamma$ which are the supplements of the true values; the incorrect angles have been copied by other writers.

*Dana (1892)*: Dana was usually fortunate in his choice of orientations; but in the case of axinite he adopted Naumann's position, giving a cell which is more oblique and indices more complicated than those of Miller.

| Dana | Peacock |
|---|---|
| *a* (100) | *l′* (1̄20) |
| *b* (010) | *a′* (1̄00) |
| *c* (001) | *c* (001) |
| *x* (111) | *x* (1̄11) |

Dana to Peacock: 1̄1̄0/200/002

*Friedel (1926)*: The last setting of axinite we need consider is that of Friedel (1926), the most consistent and persuasive exponent of the Law of Bravais. As Friedel does not discuss his orientation we cannot be sure that he found the unique lattice cell which gives the best correspondence between the relative importance of the forms and their reticular densities, a very laborious process in the triclinic system if the reticular densities are calculated from the elements. It is certain, however, that Friedel's orientation is intended to express the Law of Bravias, at least in first approximation. His cell is highly oblique and his indices are not simple, a condition which Friedel regarded as less significant than good expression of the Law of Bravais.

| Friedel | | Peacock | |
|---|---|---|---|
| *h′* | (100) | *b* | (010) |
| *g′* | (010) | *M′* | ($\bar{1}$10) |
| *p* | (001) | *r* | (011) |
| — | (111) | *i* | ($\bar{1}$31) |

Friedel to Peacock: 0$\bar{1}$0/111/001

Further orientations of axinite are those of Haüy (1822), Mohs-Haidinger (1825), Rose (1843), Hessenberg (1873), Frazier (1882), Franck (1893), and Gossner and Reichel (1932); but since these settings illustrate no principle other than those already considered they need not be discussed in detail. The selected orientations, all by eminent crystallographers of the past, illustrate the more important principles which have guided morphologists in choosing triclinic elements. If we use the normal setting, in our sense, as the criterion, then the Principle of Simplest Indices stands out as the most successful morphological principle, although it must be recognized that this principle is less useful in directly finding the desired elements than in choosing between several possible orientations. In this case also the Law of Complication leads to the proper result. On the other hand, the Law of Bravais, which often indicates the proper solution, fails to give a satisfactory setting for axinite. The Principle of Least Anorthism in its extreme form is unsuccessful and the Principle of Highest Pseudo-Symmetry likewise fails, since the structure lattice of axinite possesses no simple multiple lattice with pronounced pseudo-symmetry. Attempts to exhibit morphological analogies between axinite and other species have miscarried; and settings in which a weak zone is taken as an axial zone have proved unfortunate. Since the reported cleavages in normal setting are {100}, {001}, {110}, {011}, {010}, {$\bar{1}$01}, the Principle of Simplest Cleavages would lead in this case to normal elements; but none of the previous authors appears to have been guided exclusively by this principle. In another case the score would undoubtedly be different in detail, with the Principle of Simplest Indices still leading as the most reliable of the older methods of choosing between alternative settings.

## PROPRIETY OF THE NORMAL SETTING OF TRICLINIC CRYSTALS

The proposed setting of axinite, based on the smallest structure cell, fulfils all reasonable morphological requirements. The cleavages have the simplest possible indices; the face-symbols are likewise the simplest that can be obtained; the crystal axes approach rectangularity and the lattice cell tends to orthorhombic pseudo-symmetry as closely as is consistent with simplest indices; and the lattice cell is oriented according to existing morphological conventions. The normal setting is therefore the proper setting of axinite. The fact that there is little correspondence between the relative importance of the forms and their relative reticular densities is no argument against the normal setting, especially since no lattice will give the desired agreement. The case is one in which the Law of Bravais is inadequate, and I feel sure that both Friedel and Ungemach would have freely admitted this and accepted the normal setting with the structural evidence before them.

Conversely, if we accept the normal setting of axinite as the proper setting, the fulfillment of most of the usual morphological requirements indicates that the principles which underlie them are true, and suggests that these principles should therefore give the normal setting. But, as we have seen, these principles have led to a dozen different orientations, which show in the most convincing manner that the old rules are but partial truths leading to a variety of results according to the particular compromise struck between their variously conflicting terms.

Is the normal setting equally appropriate to triclinic species in general? A number of well-developed triclinic species have been examined with this question in mind, in each case an unprejudiced determination of the normal elements from the gnomonic projection of the observed forms being compared with the elements of the structural cell, if known. In two cases, copiapite and rosenbuschite, for which the lattice determinations were lacking, rigorous determinations were made with the Weissenberg *x*-ray goniometer. Some of the details of these studies may be given another time; suffice it here to say that the following species were examined: wollastonite, pectolite, schizolite, vogtite, rosenbuschite, rhodonite, babingtonite, aenigmatite, cyanite, chalcanthite, copiapite and plagioclase feldspar. In all but one, namely plagioclase, the smallest cell of the structure lattice proves to be eminently suitable for morphological purposes, and this cell was easily found, as in the case of axinite, by simple inspection of the gnomonic projection of the known forms. In the case of plagioclase the classical morphological lattice, which properly exhibits the marked monoclinic pseudo-symmetry of the species, corresponds to a base-centered, therefore double structural cell. In rosenbuschite the external forms are not sufficient to determine a lattice. The morphology of three further triclinic species, roemerite, quenstedtite and anapaite also clearly shows the structural lattice, but lattice determinations for these species are still lacking.

The cases examined constitute a large proportion of the known triclinic minerals occurring in well-developed crystals, a number sufficient to warrant the conclusion that the normal setting, based on the smallest structure cell, is the proper setting for triclinic crystals except when well-marked pseudo-symmetry of habit points definitely to a simple multiple lattice of the structure lattice as the better morphological framework.

All that has been said in the general case of the triclinic system applies with appropriate simplifications in the higher symmetries, in which the addition of symmetry elements progressively reduces the number of variables in the morphological elements to zero. But with increasing symmetry lattice centering becomes increasingly frequent; and since the effect of lattice centering on form development still remains to be systematically studied, the application of the normal setting will not be formally extended here beyond the triclinic system. Enough has been done, however, to indicate that the principle of normal setting will be perfectly general, and that a general procedure can be devised for distinguishing the structural lattice in the majority of cases in the gnomonic projection of the external crystal planes.

## SUMMARY

Hitherto the choice of triclinic elements has been governed by various morphological principles, which prove to be imperfect expressions of the relations of the forms of a crystal to its structural lattice, together with certain rules regulating the orientation of the chosen lattice cell. The goal uncertainly approached and sometimes reached by these principles and rules is the *normal setting*. In this setting the geometrical elements correspond to those of the simple lattice cell defined by the three shortest non-coplanar identity periods in the structural lattice; and the orientation is the unique conventional one in which $c[001]$ is the axis of the main zone of the crystal or an axis of dimetric pseudo-symmetry, $\alpha$ and $\beta$ are both obtuse, and $b[010]$ is longer than $a[100]$.

The normal elements of axinite were sought by inspecting the gnomonic projection of a single crystal; the method provisionally used involved accepting the principle of simplest indices as an approximate truth, recognizing the gnomonic projection as a two-dimensional representation of the reciprocal lattice, and taking as the first layer of the reciprocal lattice the plane lattice which accommodates most of the gnomonic projection points without systematic omissions. A direct determination of the normal elements, based on a rigorous röntgenographic

study, gave a result comparable to that obtained by the morphological method.

Eight of the existing settings of axinite are described and discussed and related to the new setting; only Miller, and after him, Victor Goldschmidt, took settings corresponding to the simple structural cell with the shortest edges.

A definitive presentation of the crystallography of axinite in the new setting is given by Palache, in a considered form which strives to meet the requirements of single-circle and two circle goniometry and introduces essential *x*-ray data.

A determination of the optical orientation of axinite agrees with published orientations. But an examination of the existing structure elements shows that they do not, as purported, define the cell with the shortest edges; the published cell-formula is also unacceptable.

It was found that the structural lattice could be discerned in the gnomonic projections of the known forms of twelve further triclinic species, and that in each case except plagioclase, the normal setting is eminently suitable for morphological description. It appears, therefore, that this setting is the proper setting for triclinic crystals, except, as in plagioclase, when well-marked pseudo-symmetry of habit demands a simple multiple lattice of the structural lattice.

The following constants were measured on a crystal of axinite from near Easton, Pennsylvania:

Elements of the structural lattice in normal setting:

$a_0 = 7.151$ Å, $b_0 = 9.184$ Å, $c_0 = 8.935$ Å; $\alpha = 91°52'$, $\beta = 98°09'$, $\gamma = 77°19'$
$a_0 : b_0 : b_0 = 0.7787 : 1 : 0.9729$;

Elements of the morphological lattice of axinite (Palache):
$a : b : c = 0.7789 : 1 : 0.9763$; $\alpha = 91°51\tfrac{1}{2}'$, $\beta = 98°04'$, $\gamma = 77°14'$

The unit cell containing $H_2B_2Al_4Ca_4(Mn, Fe)_2Si_8O_{32}$, with Mn = Fe, has the calculated density 3.316.

Optical elements (Na):

| | $\phi$ | $\rho$ | $n$ | | |
|---|---|---|---|---|---|
| $X$ | $-42°$ | 56° | 1.683 | $\pm 0.002$ | Negative |
| $Y$ | 59 | 75 | 1.688 | | $2V = 81°$ |
| $Z$ | 168 | 39 | 1.692 | | $r < v$, weak |

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## EXPLANATION OF THE FIGURES

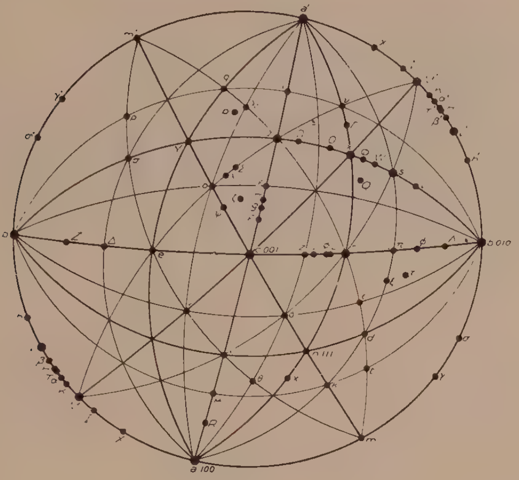
FIG. 1. Axinite. Stereographic projection of the accepted forms in normal setting.

FIG. 2. Axinite from near Easton, Pennsylvania; plan and gnomonic projection of the crystal used for geometrical, structural and optical study.

FIG. 3. Axinite. Plan and inclined view of the structure lattice showing two properly chosen cells (full lines), and one cell as given by Gossner & Reichel (dotted).

FIG. 4. Axinite. Inclined view of the studied crystal which presents the familiar aspect when viewed from the direction of (010). The greatest dimension of the crystal is 1.3 mm. The lower half of the crystal, which was attached, has been restored according to the known pinacoidal symmetry.

FIG. 5. Axinite. Relation of the axes of the optical ellipsoid ($XYZ$) and the optic axes (circles with brushes) to the principal crystal planes.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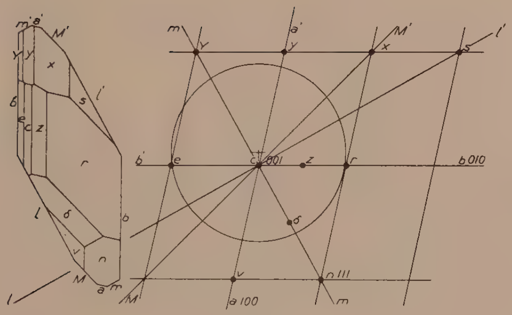
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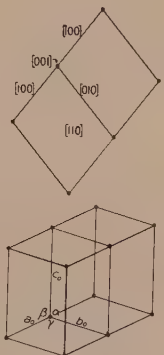
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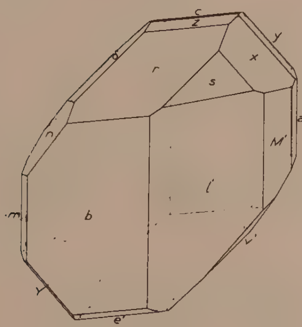
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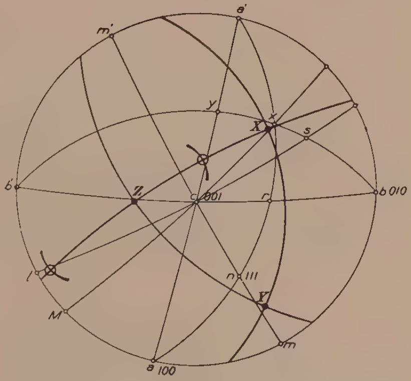
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a 100

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# APPENDIX: TRANSFORMATION OF CO-ORDINATES

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The following table of transformations enables one to pass from any setting to any other setting. It gives the face-to-face transformation (some authors only give the form-to-form transformation). The complete transformation formulae to pass from the face symbol ($hkl$) in the "old" setting to the face symbol ($pqr$) in the "new" setting are:

$$\begin{aligned} p &= \mathrm{u}\,h + \mathrm{v}\,k + \mathrm{w}\,l \\ q &= \mathrm{u}'h + \mathrm{v}'k + \mathrm{w}'l \\ r &= \mathrm{u}''h + \mathrm{v}''k + \mathrm{w}''l \end{aligned}$$

Only the coefficients need be known; they are given in matrix form in the table:

$$\begin{pmatrix} \mathrm{u} & \mathrm{v} & \mathrm{w} \\ \mathrm{u}' & \mathrm{v}' & \mathrm{w}' \\ \mathrm{u}'' & \mathrm{v}'' & \mathrm{w}'' \end{pmatrix}$$

In a text it is preferable to use the form proposed by T. V. Barker:

$$\mathrm{u\ v\ w/u'v'w'/u''v''w''}$$

Such a tabular arrangement as is presented here is compact, typographically more elegant than one giving the complete formulae. The rows and columns of the transformation matrix have known meanings: the rows [u v w], [u′ v′ w′], [u″ v″ w″], represent the "new" axes in the "old" notation; the columns (u u′ u″), (v v′ v″), (w w′ w″), represent the "old" axial planes in the "new" notation. The tabular arrangement (in the form of a matrix of matrices) lends itself to matrix calculations, affording convenient verifications.

*Multiplication of Matrices.* If the matrix "Rath to Mohs" is multiplied by the matrix "Mohs to Peacock" the resulting matrix gives the transformation "Rath to Peacock." The rule may be recalled here: in the resulting matrix the element that lies at the intersection of the $n$th column and the $m$th row is obtained by multiplying each element of the $n$th column in the first matrix by the corresponding element of the $m$th row in the second matrix and adding the three products. Matrix multiplication, in general, is not commutative.

Example:

(Rath to Mohs)·(Mohs to Peacock) = (Rath to Peacock)

$$\begin{pmatrix} 11\bar{4} \\ 3\bar{1}0 \\ 112 \end{pmatrix} \begin{pmatrix} 00\bar{2} \\ 110 \\ \bar{1}10 \end{pmatrix} = \begin{pmatrix} 1.0+3.0+1.\bar{2} & 1.0+\bar{1}.0+1.\bar{2} & \bar{4}.0+0.0+2.\bar{2} \\ 1.1+3.1+1.0 & 1.1+\bar{1}.1+1.0 & \bar{4}.1+0.1+2.0 \\ 1.\bar{1}+3.1+1.0 & 1.\bar{1}+\bar{1}.1+1.0 & \bar{4}.\bar{1}+0.1+2.0 \end{pmatrix} = \begin{pmatrix} \bar{1}\bar{1}2 \\ 20\bar{2} \\ 1\bar{1}2 \end{pmatrix}$$

TABLE OF AXINITE TRANSFORMATIONS

| To<br>From | Neumann 1825 | Hausmann 1847<br>Mohs 1824<br>Zippe 1839 | Miller (*khl*)* 1852 | Lévy 1838<br>Des Cloizeaux 1862 | vom Rath 1866 | Schrauf 1870 | Hessenberg 1873 |
|---|---|---|---|---|---|---|---|
| Neumann 1825 | 100<br>010<br>001 | $2.9.\overline{65}$<br>2.9.61<br>$\bar{7}.0.7$ | $2.9.\bar{2}$<br>$\bar{7}.0.7$<br>0.0.63 | $2.9.\overline{65}$<br>$\overline{16}.\bar{9}.79$<br>0.0.126 | $\bar{1}.6.22$<br>$\bar{7}.0.\overline{56}$<br>$\bar{3}.\bar{3}.24$ | $7.0.\overline{70}$<br>7.0.56<br>$\bar{2}.\bar{9}.2$ | $2.9.\bar{2}$<br>$\bar{7}.0.\overline{56}$<br>$\bar{7}.0.70$ |
| Hausmann 1847<br>Mohs 1824<br>Zippe 1839 | $\bar{1}.1.\overline{18}$<br>774<br>$\bar{1}10$ | 100<br>010<br>001 | 110<br>002<br>$\bar{1}10$ | 100<br>$\bar{1}02$<br>$\bar{1}10$ | 132<br>$3\bar{3}6$<br>$\bar{2}02$ | $1\bar{1}\bar{2}$<br>$\bar{1}1\bar{2}$<br>$\bar{1}\bar{1}0$ | 110<br>$1\bar{1}2$<br>$\bar{1}12$ |
| Miller (*khl*)*<br>1852 | $0\bar{9}1$<br>720<br>001 | $10\bar{1}$<br>101<br>010 | 100<br>010<br>001 | $10\bar{1}$<br>$\bar{1}21$<br>002 | 211<br>$03\bar{3}$<br>$\bar{1}11$ | $0\bar{1}\bar{1}$<br>$0\bar{1}1$<br>$\bar{1}00$ | 100<br>$01\bar{1}$<br>011 |
| Lévy 1838 Des Cloizeaux 1862 | $\bar{9}.\bar{9}.1$<br>16.2.7<br>0.0.1 | 200<br>202<br>110 | 201<br>110<br>001 | 100<br>010<br>001 | 513<br>$33\bar{3}$<br>$\bar{1}10$ | $\bar{1}\bar{1}\bar{1}$<br>$\bar{1}\bar{1}1$<br>$\bar{2}0\bar{1}$ | 201<br>$11\bar{1}$<br>111 |
| vom Rath<br>1866 | $\bar{8}.\overline{10}.\overline{16}$<br>$16.2.\overline{10}$<br>$1.\bar{1}.2$ | $11\bar{4}$<br>$3\bar{1}0$<br>112 | $20\bar{2}$<br>112<br>$1\bar{1}2$ | $11\bar{4}$<br>118<br>$2\bar{2}4$ | 100<br>010<br>001 | $\bar{1}0\bar{2}$<br>$0\bar{1}0$<br>$\bar{1}01$ | $10\bar{1}$<br>010<br>102 |
| Schrauf<br>1870 | 8.10.0<br>$\bar{2}.\bar{2}.\overline{14}$<br>$\bar{1}.1.0$ | $1\bar{1}\bar{2}$<br>$\bar{1}1\bar{2}$<br>$\bar{1}\bar{1}0$ | $00\bar{2}$<br>$\bar{1}\bar{1}0$<br>$\bar{1}10$ | $1\bar{1}\bar{2}$<br>$\bar{3}\bar{1}2$<br>$\bar{2}20$ | $\bar{1}0\bar{2}$<br>$0\bar{3}0$<br>$\bar{1}01$ | 100<br>010<br>001 | $00\bar{1}$<br>$0\bar{1}0$<br>$\bar{1}00$ |
| Hessenberg<br>1873 | $0.\overline{10}.\bar{8}$<br>$\overline{14}.2.2$<br>$0.\bar{1}.1$ | $21\bar{1}$<br>$2\bar{1}1$<br>011 | 200<br>011<br>$0\bar{1}1$ | $21\bar{1}$<br>$\bar{2}13$<br>$0\bar{2}2$ | 201<br>030<br>$\bar{1}01$ | $00\bar{1}$<br>$0\bar{1}0$<br>$\bar{1}00$ | 100<br>010<br>001 |
| Frazier<br>1882 | $0.\bar{9}.4$<br>14.2.0<br>0.0.4 | $20\bar{4}$<br>204<br>010 | 200<br>010<br>004 | $10\bar{2}$<br>$\bar{1}12$<br>004 | 414<br>$0.3.\overline{12}$<br>$\bar{2}14$ | $0\bar{1}\bar{4}$<br>$0\bar{1}4$<br>$\bar{2}00$ | 200<br>$01\bar{4}$<br>014 |
| V. Goldschmidt<br>1886 | $\bar{9}10$<br>207<br>010 | $0\bar{1}1$<br>011<br>100 | 001<br>100<br>010 | $0\bar{1}1$<br>$21\bar{1}$<br>020 | 112<br>$3\bar{3}0$<br>$11\bar{1}$ | $\bar{1}\bar{1}0$<br>$\bar{1}10$<br>$00\bar{1}$ | 001<br>$1\bar{1}0$<br>110 |
| Dana<br>1892 | $\bar{9}.\bar{9}.2$<br>16.2.0<br>0.0.2 | $20\bar{2}$<br>202<br>110 | 200<br>110<br>002 | $10\bar{1}$<br>011<br>002 | 512<br>$33\bar{6}$<br>$\bar{1}12$ | $\bar{1}\bar{1}\bar{2}$<br>$\bar{1}\bar{1}2$<br>$\bar{2}00$ | 200<br>$11\bar{2}$<br>112 |
| V. Goldschmidt<br>1897–1913 | $\bar{9}01$<br>270<br>001 | $0\bar{1}\bar{1}$<br>$0\bar{1}1$<br>100 | $0\bar{1}0$<br>100<br>001 | $0\bar{1}\bar{1}$<br>211<br>002 | $1\bar{2}1$<br>$30\bar{3}$<br>111 | $\bar{1}0\bar{1}$<br>$\bar{1}01$<br>010 | $0\bar{1}0$<br>$10\bar{1}$<br>101 |
| Friedel<br>1926 | $0\bar{9}1$<br>797<br>001 | 110<br>112<br>010 | 111<br>010<br>001 | 110<br>$\bar{1}10$<br>002 | 233<br>$03\bar{3}$<br>$\bar{1}00$ | $0\bar{1}\bar{1}$<br>$0\bar{1}1$<br>$\bar{1}\bar{1}\bar{1}$ | 111<br>$01\bar{1}$<br>011 |
| Gossner-Reichel<br>1932 | $0\bar{9}1$<br>790<br>001 | $11\bar{1}$<br>111<br>010 | 110<br>010<br>001 | $11\bar{1}$<br>$\bar{1}11$<br>002 | 231<br>$03\bar{3}$<br>$\bar{1}01$ | $0\bar{1}\bar{1}$<br>$0\bar{1}1$<br>$\bar{1}\bar{1}0$ | 110<br>$01\bar{1}$<br>011 |
| Peacock<br>1937 | 901<br>$\bar{2}70$<br>001 | $01\bar{1}$<br>011<br>$\bar{1}00$ | 010<br>$\bar{1}00$<br>001 | $01\bar{1}$<br>$\bar{2}\bar{1}1$<br>002 | $\bar{1}21$<br>$\bar{3}0\bar{3}$<br>$\bar{1}\bar{1}1$ | $10\bar{1}$<br>101<br>$0\bar{1}0$ | 010<br>$\bar{1}0\bar{1}$<br>$\bar{1}01$ |

TABLE OF AXINITE TRANSFORMATIONS (*Concluded*)

| To<br>From | Frazier 1882 | V. Goldschmidt 1886 | Dana 1892 | V. Goldschmidt 1897–1913 | Friedel 1926 | Gossner-Reichel 1932 | Peacock 1937 |
|---|---|---|---|---|---|---|---|
| Neumann<br>1825 | $4.18.\bar{4}$<br>$\overline{28}.0.28$<br>$0.0.63$ | $7.0.7$<br>$0.0.63$<br>$2.9.\bar{2}$ | $2.9.\bar{2}$<br>$\overline{16}.\bar{9}.16$<br>$0.0.63$ | $7.0.7$<br>$\bar{2}.\bar{9}.2$<br>$0.0.63$ | $9.9.\overline{72}$<br>$7.0.7$<br>$0.0.63$ | $9.9.\bar{9}$<br>$7.0.7$<br>$0.0.63$ | $7.0.7$<br>$2.9.\bar{2}$<br>$0.0.63$ |
| Hausmann 1847<br>Mohs 1824<br>Zippe 1839 | 220<br>008<br>$\bar{1}10$ | 002<br>$\bar{1}10$<br>110 | 110<br>$\bar{1}\bar{1}4$<br>$\bar{1}10$ | 002<br>$\bar{1}\bar{1}0$<br>$\bar{1}10$ | $20\bar{2}$<br>002<br>$\bar{1}10$ | $11\bar{2}$<br>002<br>$\bar{1}10$ | $00\bar{2}$<br>110<br>$\bar{1}10$ |
| Miller (*khl*)*<br>1852 | 200<br>040<br>001 | 010<br>001<br>100 | 100<br>$\bar{1}20$<br>001 | 010<br>$\bar{1}00$<br>001 | $1\bar{1}\bar{1}$<br>010<br>001 | $1\bar{1}0$<br>010<br>001 | $0\bar{1}0$<br>100<br>001 |
| Lévy 1838<br>Des Cloizeaux 1862 | 402<br>440<br>001 | 110<br>001<br>201 | 201<br>$02\bar{1}$<br>001 | 110<br>$\bar{2}0\bar{1}$<br>001 | $1\bar{1}0$<br>110<br>001 | $1\bar{1}1$<br>110<br>001 | $\bar{1}\bar{1}0$<br>201<br>001 |
| vom Rath<br>1866 | $40\bar{4}$<br>448<br>$1\bar{1}2$ | 112<br>$1\bar{1}2$<br>$20\bar{2}$ | $20\bar{2}$<br>026<br>$1\bar{1}2$ | 112<br>$\bar{2}02$<br>$1\bar{1}2$ | $00\bar{6}$<br>112<br>$1\bar{1}2$ | $1\bar{1}\bar{4}$<br>112<br>$1\bar{1}2$ | $\bar{1}\bar{1}2$<br>$20\bar{2}$<br>$1\bar{1}2$ |
| Schrauf<br>1870 | $00\bar{4}$<br>$\bar{4}\bar{4}0$<br>$\bar{1}10$ | $\bar{1}\bar{1}0$<br>$\bar{1}10$<br>$00\bar{2}$ | $00\bar{2}$<br>$\bar{2}\bar{2}2$<br>$\bar{1}10$ | $\bar{1}\bar{1}0$<br>002<br>$\bar{1}10$ | $20\bar{2}$<br>$\bar{1}10$<br>$\bar{1}10$ | $11\bar{2}$<br>$\bar{1}\bar{1}0$<br>$\bar{1}10$ | 110<br>$00\bar{2}$<br>$\bar{1}10$ |
| Hessenberg<br>1873 | 400<br>044<br>$0\bar{1}1$ | 011<br>$0\bar{1}1$<br>200 | 200<br>$\bar{1}22$<br>$0\bar{1}1$ | 011<br>$\bar{2}00$<br>$0\bar{1}1$ | $20\bar{2}$<br>011<br>$0\bar{1}1$ | $2\bar{1}\bar{1}$<br>011<br>$0\bar{1}1$ | $01\bar{1}$<br>200<br>$0\bar{1}1$ |
| Frazier<br>1882 | 100<br>010<br>001 | 010<br>004<br>200 | 100<br>$\bar{1}10$<br>002 | 010<br>$\bar{2}00$<br>004 | $2\bar{1}\bar{4}$<br>010<br>004 | $2\bar{1}0$<br>010<br>004 | $0\bar{1}0$<br>200<br>004 |
| V. Goldschmidt<br>1886 | 002<br>400<br>010 | 100<br>010<br>001 | 001<br>201<br>010 | 100<br>$00\bar{1}$<br>010 | $\bar{1}\bar{1}1$<br>100<br>010 | $\bar{1}01$<br>100<br>010 | $\bar{1}00$<br>001<br>010 |
| Dana<br>1892 | 200<br>220<br>001 | 110<br>002<br>200 | 100<br>010<br>001 | 110<br>$\bar{2}00$<br>002 | $1\bar{1}\bar{2}$<br>110<br>002 | $1\bar{1}0$<br>110<br>002 | $\bar{1}\bar{1}0$<br>200<br>002 |
| V. Goldschmidt<br>1897–1913 | $0\bar{2}0$<br>400<br>001 | 100<br>001<br>$0\bar{1}0$ | $0\bar{1}0$<br>210<br>001 | 100<br>010<br>001 | $\bar{1}\bar{1}\bar{1}$<br>100<br>001 | $\bar{1}\bar{1}0$<br>100<br>001 | $\bar{1}00$<br>$0\bar{1}0$<br>001 |
| Friedel<br>1926 | 222<br>040<br>001 | 010<br>001<br>111 | 111<br>$\bar{1}1\bar{1}$<br>001 | 010<br>$\bar{1}\bar{1}\bar{1}$<br>001 | 100<br>010<br>001 | 101<br>010<br>001 | $0\bar{1}0$<br>111<br>001 |
| Gossner-Reichel<br>1932 | 220<br>040<br>001 | 010<br>001<br>110 | 110<br>$\bar{1}10$<br>001 | 010<br>$\bar{1}\bar{1}0$<br>001 | $10\bar{1}$<br>010<br>001 | 100<br>010<br>001 | $0\bar{1}0$<br>110<br>001 |
| Peacock<br>1937 | 020<br>$\bar{4}00$<br>001 | $\bar{1}00$<br>001<br>010 | 010<br>$\bar{2}\bar{1}0$<br>001 | $\bar{1}00$<br>$0\bar{1}0$<br>001 | $11\bar{1}$<br>$\bar{1}00$<br>001 | 110<br>$\bar{1}00$<br>001 | 100<br>010<br>001 |

*Remark.* The product of any transformation matrix (say "Rath to Peacock") by the matrix of its inverse transformation ("Peacock to Rath") gives the unit matrix E, symbol of the identical transformation:

$$\begin{pmatrix} \bar{1}\bar{1}2 \\ 20\bar{2} \\ 1\bar{1}2 \end{pmatrix} \begin{pmatrix} \bar{1}21 \\ \bar{3}0\bar{3} \\ \bar{1}\bar{1}1 \end{pmatrix} = \begin{pmatrix} 100 \\ 010 \\ 001 \end{pmatrix} = \mathrm{E}$$

*Inverse Matrix.* Any transformation being given (say "Rath to Peacock") the matrix of the inverse transformation ("Peacock to Rath") is the inverse matrix. The rule may be recalled here: any element $B_{ij}$ of the inverse matrix B is given by the value of the co-factor of the element $A_{ji}$ which, in the direct matrix A, is symmetrical of $A_{ij}$ with respect to the main diagonal (upper left-lower right).

Example:

(Rath to Peacock) (Peacock to Rath)

$$A = \begin{pmatrix} \bar{1}\bar{1}2 \\ 20\bar{2} \\ 1\bar{1}2 \end{pmatrix} \qquad B = \begin{pmatrix} \bar{1}21 \\ \bar{3}0\bar{3} \\ \bar{1}\bar{1}1 \end{pmatrix}$$

Matrix calculations are of great value to crystallography. Although their use has been advocated by various authors they have not received the recognition they deserve. The purpose of this appendix is to show their simplicity and illustrate their usefulness.

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[*] Miller uses a left-handed system of coordinates, *i.e.*, in his symbol (*hkl*) the first index *h* refers to the axis that slopes to the right (the *b*-axis of a right-handed system) and the second index *k* refers to the axis that slopes forward (the *a*-axis of a right-handed system). Hence the rules: (1) Before applying any transformation "Miller to N . . ." interchange the first two indices in the Miller symbols. (2) After having applied any transformation "N . . . to Miller" interchange the first two indices of the obtained symbols.

# THE MORPHOLOGY OF GORDONITE

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At the time of the discovery of the hydrous magnesium aluminum phosphate gordonite ($MgO \cdot Al_2O_3 \cdot P_2O_5 \cdot 9H_2O$) by Larsen and Shannon (1930), the material available for a crystallographic study was of poor quality. In the fall of 1936 the original locality at Fairfield, Utah, was visited by Arthur Montgomery and Edwin Over, and a quantity of new material was collected. Subsequent examination showed far better crystals of a number of the unusual phosphates of this locality than were found in any of the material used in the original descriptions. Gordonite was one of these minerals.

The phosphates form isolated nodules up to a foot in diameter. Most are smaller, however, and lie in apparent layers in an impure shattered limestone. The nodule-bearing bands are about a foot in thickness, with the concretions irregularly distributed through the soft rock.

All of the nodules were originally composed of variscite, which, through alteration, has given rise to the many unusual and sometimes unique phosphates. Pseudowavellite and wardite are the most abundant now present, often appearing to be the final stable alteration products. During the change, shrinkage took place with resultant cavities between the residual variscite and the enveloping pseudowavellite. In these cavities solutions of fluctuating composition penetrated the nodules and permitted the formation of crystals of some of the rarer minerals. One of the most notable is the gordonite, which is attached to either face, on the variscite or the pseudowavellite. Good crystals of wardite were also found, the morphology of which will be considered in a later paper.

Gordonite is thus easily recognized in the specimens from its characteristic relation to the variscite and the pseudowavellite. When pure and free from the matrix, it develops white transparent crystals, but it is gray when attached to the pseudowavellite or variscite. Free tips of the grayish crystals are often pale pink, but the color is only noticeable in the upper extremities of the crystal bundles where the crystals grew freely. Most of the crystals are grouped together in these bundles, radiating outward in sheaf-like aggregates with all the individuals of any group similarly terminated. A few crystals are perched sideways upon other crystals and are doubly terminated. They vary in size from individuals of 0.5 to 1 mm. and aggregates up to 5 or more mm. in length, down to extremely minute crystals. Measurements were made of all types of material; the extremely minute crystals gave slightly better results than the larger ones.

The tendency toward a sheaf-like growth was revealed in the individual crystals as well as in the clusters, for it was often observed that $\rho$ readings in excess of 90° could be obtained through the entire revolution on the vertical circle. The variation was but a few minutes in most cases and presumably of no significance, aside from this characteristic.

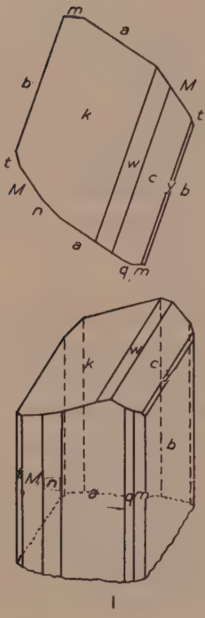

Fig. 1

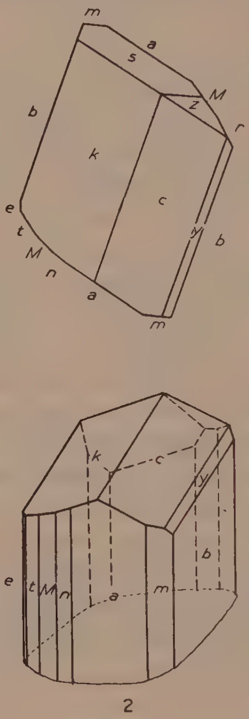

Fig. 2

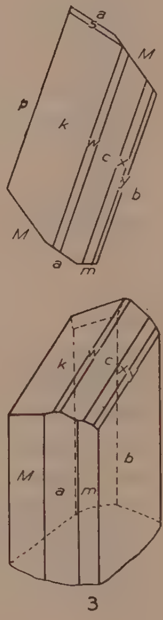

Fig. 3]

The crystals are all strongly striated and most are unsatisfactory for measurement. The main zone [001] is most strongly striated; the zone [100] is similarly marked and often gives no distinct signals. In the normal triclinic setting (Peacock, 1937) the prominent cleavage is {010}; there is also a fair cleavage {100} and a poor but distinct cleavage {001}. As shown by Larsen and Shannon (1930), gordonite resembles the chemically related triclinic species paravauxite (Gordon, 1923) in form and angles. This similarity appears in the triclinic projection elements of the two species in Gordon's setting:

Gordonite (Pough)

$$p_0'=1.496,\ q_0'=0.755;\ x_0'=0.383,\ y_0'=0.275;\ \nu=73°19\tfrac{1}{2}'$$

Paravauxite (Gordon)

$$p_0'=1.5012,\ q_0'=0.7183;\ x_0'=0.3715,\ y_0'=0.2382;\ \nu=75°15'.$$

In the normal setting the elements and indices of both species are related to Gordon's setting by the transformation:

Gordon to Pough: 100/110/001

By graphical solution the mean measurements on the common forms, *c*{001}, *b*{010}, *a*{100}, *y*{011}, *k*{$0\bar{1}1$}, *M*{$1\bar{1}0$}, give the approximate projection elements:

$$p_0{}'=1.469,\ q_0{}'=0.755;\ x_0{}'=0.383,\ y_0{}'=0.275;\ \nu=102°49'$$

leading to the polar and linear elements:

$$p_0:q_0:r_0=1.3287:0.6829:1;\ \lambda=\ 75°36',\ \mu=\ 73°35',\quad \nu=102°49',$$
$$a:b:c:=0.5192:1:0.6942;\ \alpha=109°27',\ \beta=110°57\tfrac{1}{2}',\ \gamma=\ 71°40\tfrac{1}{2}'$$

Table 1 summarizes the measurements on thirteen crystals of gordonite; table 2 is a formal angle-table for the accepted forms. It will be seen that the calculated co-ordinate angles mostly lie well within the measured range. In addition to the nineteen accepted forms, measurements were obtained corresponding roughly to the symbols {510}, {$4\bar{7}0$}, {$1\bar{4}0$}, {$\bar{1}01$}, {$\bar{2}\bar{1}1$}. These must be regarded as uncertain forms until better measurements are made.

Table 1. Gordonite: Two-Circle Measurements on Thirteen Crystals

| Forms | No. of faces | Measured Range | | Measured Mean | |
|---|---|---|---|---|---|
| | | φ | ρ | φ | ρ |
| *c* 001 | 10 | 53°18′– 56°17′ | 24°22′–26°00′ | 54°47′t | 25°14′ |
| *b* 010 | 26 | — | — | 0 00 | 90 00 |
| *a* 100 | 12 | 104 14 –101 13 | — | 102 49 | 90 00 |
| *m* 110 | 7 | 74 02 – 75 05 | — | 74 47 | 90 00 |
| *j* $5\bar{1}0$ | 1 | — | — | 108 00 | 90 00 |
| *p* $4\bar{1}0$ | 2 | 110 06 –110 32 | — | 110 19 | 90 00 |
| *i* $3\bar{1}0$ | 2 | 111 09 –112 30 | — | 111 50 | 90 00 |
| *n* $2\bar{1}0$ | 3 | 114 46 –117 18 | — | 116 22 | 90 00 |
| *l* $3\bar{2}0$ | 2 | 118 19 –119 54 | — | 119 06 | 90 00 |
| *M* $1\bar{1}0$ | 17 | 126 07 –129 03 | — | 127 07 | 90 00 |
| *r* $2\bar{3}0$ | 2 | 134 16 –135 44 | — | 135 00 | 90 00 |
| *t* $1\bar{2}0$ | 6 | 141 05 –143 04 | — | 142 46 | 90 00 |
| *d* $1\bar{3}0$ | 3 | 149 35 –150 33 | — | 150 05 | 90 00 |
| *f* $1\bar{5}0$ | 1 | — | — | 161 11 | 90 00 |
| *e* $1\bar{7}0$ | 4 | 164 18 –166 08 | — | 165 13 | 90 00 |
| *x* 013 | 1 | 37 08 – 38 18 | 32 10 –32 25 | 37 43 | 32 18 |
| *y* 011 | 4 | 19 15 – 22 33 | 46 03 –48 50 | 20 47 | 47 51 |
| *w* $0\bar{5}6$ | 4 | 133 05 –135 35 | 26 53 –27 47 | 134 03 | 27 21 |
| *k* $0\bar{1}1$ | 11 | 139 14 –146 54 | 30 52 –33 02 | 141 42 | 31 20 |

TABLE 2. GORDONITE—$MgO \cdot Al_2O_3 \cdot P_2O_5 \cdot 9H_2O$
Triclinic; pinacoidal—$\bar{1}$
$a:b:c = 0.5192:1:0.6942$; $\alpha = 109°27'$, $\beta = 110°57\frac{1}{2}'$, $\gamma = 71°40\frac{1}{2}'$
$p_0:q_0:r_0 = 1.3287:0.6829:1$; $\lambda = 75°36'$, $\mu = 73°35'$, $\nu = 102°49'$
$p_0' = 1.469$, $q_0' = 0.755$; $x_0' = 0.383$, $y_0' = 0.275$

| Forms | $\varphi$ | $\rho$ | *A* | *B* | *C* |
|---|---|---|---|---|---|
| *c* 001 | 54°19½′ | 25°14½′ | 73°35′ | 75°36′ | 0°00′ |
| *b* 010 | 0 00 | 90 00 | 102 49 | 0 00 | 75 36 |
| *a* 100 | 102 49 | 90 00 | 0 00 | 102 49 | 73 35 |
| *m* 110 | 73 19½ | 90 00 | 29 28½ | 73 19½ | 66 13 |
| *j* $5\bar{1}0$ | 108 25 | 90 00 | 5 36 | 108 25 | 75 31 |
| *p* $4\bar{1}0$ | 109 46 | 90 00 | 6 57 | 109 46 | 76 00 |
| *i* $3\bar{1}0$ | 111 57½ | 90 00 | 9 08½ | 111 57½ | 76 48½ |
| *n* $2\bar{1}0$ | 116 09 | 90 00 | 13 20 | 116 09 | 78 23 |
| *l* $3\bar{2}0$ | 120 04 | 90 00 | 17 15 | 120 04 | 79 54½ |
| *M* $1\bar{1}0$ | 127 02½ | 90 00 | 24 13½ | 127 02½ | 82 41 |
| *r* $2\bar{3}0$ | 135 31 | 90 00 | 32 42 | 135 31 | 86 15½ |
| *t* $1\bar{2}0$ | 142 02½ | 90 00 | 39 13½ | 142 02½ | 89 01½ |
| *d* $1\bar{3}0$ | 151 04 | 90 00 | 48 15 | 151 04 | 92 52 |
| *f* $1\bar{5}0$ | 160 45 | 90 00 | 57 56 | 160 45 | 96 56½ |
| *e* $1\bar{7}0$ | 165 40½ | 90 00 | 62 51½ | 165 40½ | 98 56 |
| *x* 013 | 36 01½ | 33 04½ | 77 35 | 63 48½ | 11 47 |
| *y* 011 | 20 24 | 47 42 | 84 24 | 46 07 | 29 29 |
| *w* $0\bar{5}6$ | 132 45½ | 27 33 | 66 22½ | 108 18 | 32 42 |
| *k* $0\bar{1}1$ | 141 25 | 31 33 | 65 51½ | 114 08½ | 38 33 |

In the vertical zone, the dominant form is *b*{010}, which has broad faces giving somewhat confused signals in most cases, because of the outwardly curving surface already mentioned and other irregularities. The luster on this surface is pearly, as in paravauxite; this, together with the prominent cleavage {010}, makes orientation of the crystals easy.

The form next in frequency in the vertical zone is *a*{100}, which, in combination with *b*{010}, determines the outlines of the crystals. The form *a* is about half as frequent as *b*; it is rarely plane, and usually shows a series of striations parallel to the prism edges, resulting in a train of reflections rather than a single sharp signal. A brilliant signal comes in the proper place in the train, however.

Equally common in occurrence is *M*{$1\bar{1}0$}, which is often the same size as *a* and similar in appearance. It is likewise striated, and exact measurement is not easy. This is probably the form to which Larsen refers in his brief angle-table as $\{490\}$.

The form $t\{1\bar{2}0\}$ is much rarer and usually narrower than $M$ and $a$. It is also striated vertically and gives a train of reflections in which the reflection from $(1\bar{2}0)$ stands out as a sharp signal on many of the crystals. In gordonite, as in paravauxite, all of the vertical planes except $m$ lie in the negative quadrants (2 and 4). Since the symbolization of a large number of complex forms would be quite futile, only the simpler and more prominent ones have been accepted. Most of these were observed several times in fair position on different crystals. The symbols of the vertical zone do not conform to the normal complication series of Goldschmidt; they do, however, exactly fit the Harmonic-Arithmetic series of Peacock (1936), thus indicating that the chosen vertical axial planes are axial planes of the structural lattice.

On the terminations the base is sometimes lacking, the entire crystal being truncated by a large face $k\{0\bar{1}1\}$. The face is plane, usually without striations, and gives excellent signals. Next in frequency and importance in this zone is the $c\{001\}$, which is rarely as large as $k$. It is often striated parallel to its intersection with $b$ and $k$. Third in frequency in this zone is $y\{011\}$, which, though frequently present, is invariably a narrow line form, giving a poor signal. Sometimes the termination of a gordonite crystal resembles the vertical zone in the multiplicity of its striations, a continuous train of reflections extending from $c$, rarely even from $k$, to $y$. Two more forms were observed several times in this train, $w\{0\bar{5}6\}$ and $x\{013\}$. Both were present as distinct forms, but only on the crystals presenting the strongly striated terminations. The terminal forms $s\{\bar{2}\bar{1}1\}$ and $z\{\bar{1}01\}$ are very rare. The form $s\{\bar{2}\bar{1}1\}$, already observed by Larsen and Shannon, was found on several crystals in one radiating aggregate; $z\{\bar{1}01\}$ was seen once as a small face.

Many crystals of gordonite are terminated wholly by $k\{0\bar{1}1\}$. Another common habit is shown in fig. 1. The habit shown in fig. 2 is rare. The usual appearance of crystals with $s\{\bar{2}\bar{1}1\}$ is shown in fig. 3 in which $s$ appears as a large pyramidal face truncating the edge between $k$ and $a'$.

The writer acknowledges the assistance he has received from Dr. M. A. Peacock, who indicated the normal setting of this triclinic mineral and revised the paper, and to Mr. C. W. Wolfe, who calculated the elements and angles in table 2.

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# ON BABINGTONITE

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The granite pegmatites of Blueberry Mountain, Woburn, Massachusetts, contain small veins filled with calcite and lined with excellent crystals of the rare mineral babingtonite, a metasilicate of lime and iron with essential hydroxyl, which has generally been classed as a triclinic pyroxene. The occurrence and appearance of these crystals have been described in a recent paragenetic study (1937); the object of the present paper is to record the results of a more detailed morphological, roentgenographic and optical study which leads to a definitive statement of the crystallography of the species and points to its systematic relations.

In a recent paper on axinite Peacock (1937) has proposed a unique setting for triclinic crystals, named the *normal setting*, which conforms to generally accepted morphological and structural requirements. In this setting the lattice elements correspond to the simple cell defined by the three shortest non-coplanar identity periods of the structural lattice, in the one position out of twenty-four in which the vertical cell-edge is the axis of the main morphological zone, the axial angles $\alpha$ and $\beta$ are both obtuse, and the axial length $b[010]$ is longer than the axial length $a[100]$. Peacock shows how this unique setting can be reached by inspection of the gnomonic projection of the crystal forms on the plane normal to the axis of the main zone; and he proves the validity of the method in the case of axinite by showing that an independent determination of the structural lattice leads to absolute elements which are geometrically similar to those obtained from the morphology. The newly found babingtonite crystals afford an opportunity to apply Peacock's procedure for finding the normal setting and test the propriety of this setting in another typical case.

*The normal setting of babingtonite.* Crystals suitable for morphological, structural and optical study were obtained by dissolving the calcite matrix in hydrochloric acid. The residue yielded babingtonite crystals ranging from 0.1 mm. to 1.0 mm. in size. The crystals are black with bright faces giving good reflections. The smallest crystals, all of which are doubly terminated, proved most suitable for study; they are short-prismatic in habit, somewhat flattened parallel to the axis of elongation, and richer in forms than the crystals of larger size. The axis of the zone of prismatic development is also the axis of the zone which is most commonly the main zone of babingtonite; this zone is therefore properly set vertically.

Figure 1 gives a gnomonic projection of the known forms of babingtonite on the plane normal to the chosen vertical axis. The plane of the gnomonic projection is considered as the first layer $|hk1|$ of the reciprocal lattice. Vertical planes $(hk0)$ are represented by radial lines drawn from $c(001)$ to $(hk1)$, the point $(hk1)$ being inserted as a blank point, as in *m f j h*, when it does not represent a known terminal form. The radial lines are thus normal to the respective vertical planes, and their lengths are inversely proportional to the spacings and reticular densities of the corresponding planes in the direct lattice.

The reciprocal structural lattice is determined when we have properly distinguished the first layer points $(hk1)$, which are actually in the plane of the gnomonic projection, from the higher layer points $(hkn)$ which appear in fractional positions on the plane of the gnomonic projection. This is simply done, in the present case, by taking as the first layer points those points which form a plane lattice without systematic omissions. This condition permits of only one choice: the large filled points *c r q d n s o p e k* must be the first layer points; the small blank points *y x v w u i t*, all of which represent weak forms, are therefore points in higher layers of the reciprocal lattice.

To obtain the desired representative lattice cell, whose axial planes are the three non-tautozonal planes with the greatest spacings, and whose respective reciprocal lattice points are therefore the three non-colinear points nearest the origin, we choose the first-layer point nearest the center *c*, as the axial plane (001); the first-layer point nearest to *c*, namely *d*, is taken as (011); the next nearest, not in the zone [*cd*], namely *r*, is taken as (101). All the points in the projection can now be immediately indexed; and the chosen cell meets the stated conditions. The vertical axis is the axis of the main zone; the pole of the base lies in the first quadrant, hence $\alpha$ and $\beta$ are both obtuse; and the reciprocal lattice period $q_0'=c-d$ is less then the period $p_0'=c-r$ giving $b[010]$ greater then $a[100]$. The chosen cell, therefore, stands in the unique orientation of the normal setting. If this had not been the case, the desired orientation would be reached by turning the projection about the vertical axis, or by inverting it and then turning it into the one position in which the stated conditions are satisfied.

In the normal position two circle measurements on fifteen crystals give the projection elements:

$$p_0'=0.9273,\ q_0'=0.5934;\ x_0'=0.0671,\ y_0'=0.0456;\ \nu=75°42\tfrac{1}{2}'$$

which give, by calculation, the following polar and linear elements:

$$p_0:q_0:r_0=0.9242:0.5915:1;\ \lambda=87°23\tfrac{1}{2}',\ \mu=85°38',\ \nu=75°42\tfrac{1}{2}'$$
$$a:b:c=0.6411:1:0.5747;\ \alpha=91°28',\ \beta=94°12',\ \gamma=104°11'.$$

Figure 2 shows a typical babingtonite crystal from Woburn, drawn in the position corresponding to the normal setting. The position is in every way satisfactory. The largest planes are *m*(110), *a*(100), *M*($1\bar{1}0$). The base *c*(001) is also fairly large. The side-pinacoid, *b*(010) is narrow; but this is one of the vagaries of morphological development for which there is no explanation and which should not influence the choice of elements. Even if the side-pinacoid had been absent, the above method for finding the normal setting would have led to the same result. The cleavages are {001} perfect, and {$1\bar{1}0$} imperfect, which correspond respectively to the third and fourth greatest lattice spacings. The most common morphological elongation is in the direction of the shortest axis *c*[001], and therefore in the direction of the densest lattice row.

In the normal setting the forms observed on the crystals studied are: *c*{001}, *b*{010}, *a*{100}, *m*{110}, *f*{210}, *M*{$1\bar{1}0$}, *h*{$1\bar{2}0$}, *d*{011}, *n*{$0\bar{1}1$}, *r*{101}, *q*{$\bar{1}01$}, *s*{$1\bar{1}1$}, *o*{$\bar{1}11$}, *p*{$\bar{1}21$}, the new forms: *j*{310}, *e*{$\bar{1}\bar{1}1$}, *k*{$\bar{1}\bar{2}1$}; and the new but uncertain forms: {$3\bar{5}0$}, {121}.

The prominent forms are *a c m f M h d n q s o*, most of which occur on all the crystals. The new forms, *j e k*, appear as small faces in good position, as shown by the agreement in Table 1. The two uncertain forms were observed only once each.

TABLE 1. BABINGTONITE: NEW FORMS

| Form | Number of faces | Measured | | Calculated | |
|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | $\phi$ | $\rho$ |
| *j*(310) | 3 | 64°35′ | 90°00′ | 64°42′ | 90°00′ |
| *e*($\bar{1}\bar{1}1$) | 5 | −133 42 | 48 49 | −133 02½ | 48 38½′ |
| *k*($\bar{1}\bar{2}1$) | 3 | −148 24 | 58 22 | −148 45 | 58 00 |

*Correlation of morphological settings.* Babingtonite has been variously oriented by Dauber (1855), Dana (1892) and Goldschmidt (1897–1922). Dauber's position, which was adopted by Palache & Frapie (1902) and by Palache & Gonyer (1932) refers to a cell of the structural lattice; but the choice and orientation of the cell does not conform to the normal triclinic setting. The relation of Dauber's setting to the normal setting, in the gnomonic projection and the direct lattice, is shown in figures 3, 4, in which the dotted cells and underlined symbols are those of Dauber. The settings of Goldschmidt and Dana were intended to bring out morphological analogies, and they depart even farther from the normal setting. The elements and indices of the four settings (Dauber, Dana, Goldschmidt, Richmond) are related by the transformation formulas in

Table 2, which is arranged in a double-entry form suggested by Professor J. D. H. Donnay.

TABLE 2. BABINGTONITE: TRANSFORMATION FORMULAS

| From<br>To | Dauber (1855) | Dana (1892) | Goldschmidt (1897) | Richmond |
|---|---|---|---|---|
| Dauber |  | $0\ 0\ \bar{4}$<br>$\bar{1}\ \bar{1}\ 0$<br>$\bar{1}\ 1\ 0$ | $0\ 0\ 1$<br>$1\ 0\ 0$<br>$0\ 1\ 0$ | $1\ 1\ 0$<br>$\bar{1}\ 0\ 0$<br>$0\ 0\ 1$ |
| Dana | $0\ \bar{2}\ \bar{2}$<br>$0\ \bar{2}\ 2$<br>$\bar{1}\ 0\ 0$ |  | $\bar{2}\ \bar{2}\ 0$<br>$\bar{2}\ 2\ 0$<br>$0\ 0\ \bar{1}$ | $2\ 0\ \bar{2}$<br>$2\ 0\ 2$<br>$\bar{1}\ \bar{1}\ 0$ |
| Goldschmidt | $0\ 1\ 0$<br>$0\ 0\ 1$<br>$1\ 0\ 0$ | $\bar{1}\ \bar{1}\ 0$<br>$\bar{1}\ 1\ 0$<br>$0\ 0\ \bar{4}$ |  | $\bar{1}\ 0\ 0$<br>$0\ 0\ 1$<br>$1\ 1\ 0$ |
| Richmond | $0\ \bar{1}\ 0$<br>$1\ 1\ 0$<br>$0\ 0\ 1$ | $1\ 1\ 0$<br>$\bar{1}\ \bar{1}\ \bar{4}$<br>$\bar{1}\ 1\ 0$ | $\bar{1}\ 0\ 0$<br>$1\ 0\ 1$<br>$0\ 1\ 0$ |  |

To show how this table is used to find the indices ($h'k'l'$) in a desired setting from the given indices ($h\ k\ l$) in another setting, let us transform Dana's $f\{\bar{4}\bar{4}3\}$ to Richmond's setting. From Table 2 the required transformation formula, from Dana to Richmond, is: $110/\bar{1}\bar{1}\bar{4}/\bar{1}10$. Then $h'=1\times\bar{4}+1\times\bar{4}+0\times 3=\bar{8}$; $k'=\bar{1}\times\bar{4}+\bar{1}\times\bar{4}+\bar{4}\times 3=\bar{4}$; $l'=\bar{1}\times\bar{4}+1\times\bar{4}+0\times 3=0$. The new indices are thus ($\bar{8}\bar{4}0$) or ($\bar{2}\bar{1}0$) which is a plane of our form $f\{210\}$.

Table 3 shows the forms of babingtonite observed or recorded by Dauber, Dana, Goldschmidt, Palache, Richmond, and correlates the signatures of the several authors.

Transforming the elements of Dauber to the normal setting, according to the transformation formula: from Dauber to Richmond: $0\bar{1}0/110/001$, we obtain:

$$a:b:c=0.6417:1:0.5746;\ \alpha=91°31',\ \beta=93°51',\ \gamma=104°04'$$

The elements from the new measurements are:

$$a:b:c=0.6411:1:0.5747;\ \alpha=91°28',\ \beta=94°12',\ \gamma=104°11'$$

The two sets of elements agree so closely that Dauber's transformed values are adopted in the formal angle-table for the known forms of babingtonite in the normal setting (Table 4).

*Optics*. The optical properties of the Woburn babingtonite were determined on small crystals mounted on the universal stage, and by the immersion of fragments. Due to the excessively strong absorption of the mineral it proved difficult, yet possible, to find crystals small enough to pass light, but not so small as to prevent reliable measurements on the traces of a sufficient number of the crystal planes. The optical data obtained are summarized in Table 5, in which the co-ordinate angles for the ellipsoid axes refer to the same pole and prime meridian as that used for the crystal faces. The optical orientation and the positions of the

TABLE 3. BABINGTONITE: CORRELATION OF FORM LETTERS

| | | Dauber (1855) | Dana (1892) | Goldschmidt (1897–1922) | Palache (1902–1932) | Richmond |
|---|---|---|---|---|---|---|
| *c* | 001 | *c* | *M* | *c* | *c* | *c* |
| *b* | 010 | *a* | *c* | *a* | *a* | *b* |
| *a* | 100 | — | — | *k* | *k* | *a* |
| *m* | 110 | *g* | *g* | *r* | *g* | *m* |
| *f* | 210 | — | *f* | *l* | *f* | *f* |
| *j* | 310 | — | — | — | — | *j** |
| *M* | $1\bar{1}0$ | *b* | *m* | *b* | *b* | *M* |
| *h* | $1\bar{2}0$ | *h* | *h* | *q* | *h* | *h* |
| *y* | 025 | — | — | *y* | *y* | — |
| *x* | 035 | — | — | *x* | *x* | — |
| *d* | 011 | *d* | *d* | *d* | *d* | *d* |
| *n* | $0\bar{1}1$ | — | — | *n* | *n* | *n* |
| *r* | 101 | — | — | — | *r* | *r* |
| *q* | $\bar{1}01$ | — | — | — | *q* | *q* |
| *e* | $\bar{1}\bar{1}1$ | — | — | — | — | *e** |
| *s* | $1\bar{1}1$ | *s* | *b* | *s* | *s* | *s* |
| *o* | $\bar{1}11$ | *o* | *a* | *o* | *o* | *o* |
| *w* | $\bar{2}25$ | — | — | *w* | *w* | — |
| *v* | $\bar{3}35$ | — | — | *v* | *v* | — |
| *u* | $\bar{5}54$ | — | — | *u* | *u* | — |
| *i* | $1\bar{2}2$ | — | — | *i* | *i* | — |
| *t* | $\bar{1}22$ | — | — | *t* | *t* | — |
| *k* | $\bar{1}\bar{2}1$ | — | — | — | — | *k** |
| *p* | $\bar{1}21$ | — | — | *p* | *p* | *p* |

optic axes are represented stereographically in figure 6. There is no pseudo-symmetry in the orientation, which is in keeping with the lack of pseudo-symmetry in the crystal lattice and the absence of twinning in babingtonite. For comparison with the new orientation we give the orientation obtained on crystals from Arendal, Norway, by Washington & Merwin (1923), transformed to the adopted crystal setting. The agree-

TABLE 4. BABINGTONITE—$Ca_2Fe''Fe'''Si_5O_{14}(OH)$

Triclinic; pinacoidal—$\bar{1}$

$a:b:c=0.6417:1:0.5746$; $\alpha=91°31'$, $\beta=93°51'$, $\gamma=104°04'$

$p_0:q_0:r_0=0.9227:0.5910:1$; $\lambda=87°28\tfrac{1}{2}'$, $\mu=85°39'$, $\nu=75°49\tfrac{1}{2}'$

$p_0'=0.9257$, $q_0'=0.5929$; $x_0'=0.0673$, $y_0'=0.0443$

| Forms | | $\phi$ | $\rho$ | $A$ | $B$ | $C$ |
|---|---|---|---|---|---|---|
| *c* | 001 | 56°39½′ | 4°36½′ | 85°39′ | 87°28½′ | 0°00′ |
| *b* | 010 | 0 00 | 90 00 | 75 49½ | 0 00 | 87 28½ |
| *a* | 100 | 75 49½ | 90 00 | 0 00 | 75 49½ | 85 39 |
| *m* | 110 | 47 36 | 90 00 | 28 13½ | 47 36 | 85 27 |
| *f* | 210 | 59 46 | 90 00 | 16 03½ | 59 46 | 85 24 |
| *j* | 310 | 64 42 | 90 00 | 11 07½ | 64 42 | 85 26½ |
| *M* | $1\bar{1}0$ | 112 11½ | 90 00 | 36 32 | 112 11½ | 87 24½ |
| *h* | $1\bar{2}0$ | 136 54 | 90 00 | 61 04½ | 136 54 | 89 13 |
| *y* | 025 | 13 27 | 16 08½ | 82 35½ | 74 19 | 13 09½ |
| *x* | 035 | 9 33 | 22 05 | 81 18 | 68 14½ | 19 14 |
| *d* | 011 | 6 02½ | 32 39 | 79 15½ | 57 33½ | 29 55 |
| *n* | $0\bar{1}1$ | 173 00½ | 28 56 | 93 28 | 118 41½ | 31 13½ |
| *r* | 101 | 74 19 | 45 03½ | 44 57½ | 78 58 | 40 41½ |
| *q* | $\bar{1}01$ | −102 23½ | 40 22 | 130 21 | 97 59 | 44 41½ |
| *e* | $\bar{1}\bar{1}1$ | −133 02½ | 48 38½ | 131 06 | 120 49 | 53 11 |
| *s* | $1\bar{1}1$ | 108 27 | 45 29 | 53 05½ | 103 02½ | 42 45½ |
| *w* | $\bar{2}25$ | −56 49 | 19 13 | 102 53 | 79 37½ | 31 37½ |
| *v* | $\bar{3}35$ | −60 44½ | 28 22½ | 111 11½ | 76 34 | 30 45 |
| *o* | $\bar{1}11$ | −63 41½ | 42 48½ | 121 07 | 72 28½ | 45 16½ |
| *u* | $\bar{5}54$ | −64 32½ | 49 26 | 125 48½ | 70 56½ | 51 55½ |
| *i* | $1\bar{2}2$ | 130 08½ | 34 01½ | 70 57½ | 111 09 | 32 58½ |
| *t* | $\bar{1}22$ | −36 04 | 32 56½ | 101 42 | 63 55½ | 33 26½ |
| *k* | $\bar{1}\bar{2}1$ | −148 45 | 58 00 | 127 10 | 136 28 | 62 11 |
| *p* | $\bar{1}21$ | −39 36½ | 52 29 | 109 50½ | 52 20 | 53 07½ |

ment in these independently determined orientations is satisfactory and is in accord with the noteworthy constancy in the chemical composition of the species.

Table 5. Babingtonite: Optical Elements

| | | | Washington & Merwin | | | | |
|---|---|---|---|---|---|---|---|
| | $\phi$ | $\rho$ | $\phi$ | $\rho$ | $n$(Na) | | |
| $X$ (dark green) | −104° | 46° | −104° | 44° | 1.720 | | Positive |
| $Y$ (lilac) | 145 | 70 | 145 | 71 | 1.731 | ±0.003 | $2V=76\pm2°$ |
| $Z$ (brown) | 39 | 51 | 40 | 53 | 1.753 | | $r>v$ strong |

None of the principal optical directions is nearly normal to a prominent form. An optic axis can, however, always be seen inclined at 10° to the normal to the basal cleavage.

*Structural lattice.* The structural lattice of babingtonite was determined on a small crystal from Woburn, by a method which is entirely independent of the known morphology. Rotation and equator Weissenberg photographs were taken with copper radiation about three zone-axes, giving values for three non-coplanar lattice periods, three pairs of values for the spacings of the provisional axial planes, and three accurately measurable values for the reciprocal axial angles. A study of the lattice parameters thus obtained showed that the three chosen axes of rotation, which were the previously chosen crystallographic axes, were also the directions of three shortest non-coplanar lattice periods. The lattice constants measured and computed from the $x$-ray photographs are given in Table 6.

Table 6. Babingtonite: Structural Lattice Constants

| From rotation photographs | From Weissenberg photographs | | | | |
|---|---|---|---|---|---|
| Å | Å | | | Å | |
| $a_0=$ 7.36 | $d_{100}=$ 7.16 | $a^*=0.2150$ | $\alpha^*=87°12'$ | $a_0=$ 7.39 | $\alpha=$ 91°48′ |
| $b_0=11.52$ | $d_{010}=11.18$ | $b^*=0.1377$ | $\beta^*=85°39'$ | $b_0=11.52$ | $\beta=$ 93°48′ |
| $c_0=$ 6.58 | $d_{001}=$ 6.60 | $c^*=0.2332$ | $\gamma^*=75°56'$ | $c_0=$ 6.61 | $\gamma=103°54'$ |

The above structural cell elements refer to the unique orientation fixed by the previously stated morphological conventions. The direct lattice elements obtained from the Weissenberg photographs give the following ratio, which agrees well with the previously determined geometrical elements:

$$a_0:b_0:c_0=0.642:1:0.574;\ \alpha=91°48',\ \beta=93°48',\ \gamma=103°54'$$
$$a:b:c=0.6411:1:0.5747;\ \alpha=91°28',\ \beta=94°12',\ \gamma=104°11'.$$

This agreement shows that the geometrical equivalent of the structural lattice was correctly discerned in the gnomonic projection of the external planes. It will be observed that the shortest cell-edge is the vertical axis $c[001]$, the longest cell-edge is the lateral axis $b[010]$. This relation generally obtains when a simple triclinic lattice cell is oriented according to morphological conventions; and it might well form the basis of a rule for orienting triclinic cells in cases of poor or variable crystal development.

*Structural lattice of Gossner & Mussgnug.* These authors (1928) determined the structural lattice of a crystal of babingtonite from Arendal, by measuring the identity periods in several lattice rows whose angular relations were known from the geometrical crystallography. The setting of Gossner & Mussgnug is related to the normal setting by the transformation, Gossner & Mussgnug to Richmond: $010/0\bar{1}\bar{1}/\bar{1}00$. The relation of their unit cell to ours is shown in figure 5 which gives two cells of the normal setting (elements: $a\ b\ c\ \alpha\ \beta\ \gamma$) in full lines, and one cell of Gossner & Mussgnug (elements: $a'\ b'\ c'\ \alpha'\ \beta'\ \gamma'$) in dotted lines. Corresponding identity periods in the structural lattices compare as follows:

| Gossner & Mussgnug | Richmond |
|---|---|
| $a[\bar{1}00]=$ 6.73Å | $c[001]=$ 6.61Å |
| $b[010]=$ 7.54 | $a[100]=$ 7.39 |
| $[0\bar{1}\bar{1}]=$11.83 (calc.) | $b[010]=$11.52 |
| $c[001]=$12.43 | $[\bar{1}10]=$12.10 (calc.) |

Apart from a systematic difference of about three per cent in the two sets of values, due perhaps to differences in materials and methods, the agreement is good. The four periods are the four shortest non-coplanar periods in the structural lattice. Both sets of values show that the vertical period of Gossner & Mussgnug, $c[001]$, is the fourth-shortest period, and is therefore improperly chosen according to the structural convention which Gossner clearly recognizes and often emphasizes.

*Content of the unit cell.* Five superior analyses of babingtonite are given by Palache & Gonyer (1932), four from localities in Massachusetts (by Gonyer) and one from Arendal, the type locality (by Washington). From these analyses, which show little variation, Palache and Gonyer deduce the empirical formula: $Ca_2Fe''Fe'''Si_5O_{14}(OH)$, which accepts hydroxyl as essential, neglects the small reported amounts of Ti, Al, Mn, Mg, Na+K, and agrees well with the found proportions of the main constituents. From the cell determination of Gossner & Mussgnug (1928)

Palache and Gonyer found that the unit cell of babingtonite contains two of the above empirical molecules. Since this cell content widely differs from that proposed by Gossner & Mussgnug it is desirable to make a count of the atoms of the unit cell, using the new cell elements together with the available analyses and corresponding density values.

The volume of the unit cell of babingtonite is $V_0=a_0b_0c_0/(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma-2\cos\alpha\cdot\cos\beta\cdot\cos\gamma)=545$ cubic Å. The molecular weight of the unit cell is $M_0=Vd/A=1112$, which varies slightly with the measured densities. From the given percentage weight of an oxide in an analysis in which the values are reduced to the sum of 100, the number of atoms of an element in the unit cell is $N=mM_0n/100$, where $m$ is the molecular proportion of the oxide containing the element, and $n$ is the number of atoms of the element in the oxide. Table 7 gives the values of $N$ obtained in this way from the five analyses of babingtonite, which are numbered as in Palache & Gonyer (1932).

Table 7. Babingtonite: Content of the Unit Cell

| Analysis | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Density | 3.368 | | 3.369 | | 3.340 | | 3.342 | | 3.359 | |
| | $N$ | | $N$ | | $N$ | | $N$ | | $N$ | |
| Si | 9.73 | | 9.73 | | 9.65 | | 9.59 | | 9.79 | |
| Al | 0.04 | 9.77 | 0.04 | 9.77 | — | 9.65 | 0.02 | 9.61 | 0.18 | 9.97 |
| Ti | — | | — | | — | | 0.04 | | 0.04 | |
| Fe''' | 2.04 | 2.04 | 2.02 | 2.02 | 2.02 | 2.02 | 1.88 | 1.92 | 1.86 | 1.90 |
| Fe'' | 1.45 | | 1.57 | | 1.56 | | 1.66 | | 1.19 | |
| Mn | 0.19 | 1.91 | 0.17 | 1.92 | 0.18 | 1.87 | 0.12 | 1.94 | 0.31 | 1.76 |
| Mg | 0.27 | | 0.18 | | 0.13 | | 0.17 | | 0.26 | |
| Ca | 3.92 | 3.96 | 3.91 | 3.92 | 3.90 | 3.96 | 4.00 | 4.02 | 3.68 | 3.82 |
| Na+K | 0.04 | | 0.01 | | 0.06 | | 0.02 | | 0.14 | |
| H | 1.50 | 1.50 | 1.58 | 1.58 | 1.52 | 1.52 | 1.64 | 1.64 | 1.14 | 1.14 |
| Oxygen | | 29.18 | | 29.18 | | 28.89 | | 28.89 | | 28.80 |

1. Winchester Highlands (Woburn), Mass.; anal. Gonyer.
2. Holyoke, Mass.; anal. Gonyer.
3. Deerfield, Mass.; anal. Gonyer.
4. Somerville, Mass.; anal. Gonyer. Analyses 1–4 in Palache & Gonyer (1932).
5. Arendal, Norway; anal. Washington in Washington & Merwin (1923).

Allowing a systematic increase of about three per cent in values of $N$, neglecting Al, Ti, Na+K, as unessential, and taking the H number as 2, babingtonite contains thirty atoms of oxygen in the unit cell, and the cell formula is:

$$Fe_2'''Fe_2''Ca_4Si_{10}O_{28}(OH)_2$$

in which Fe''' may be associated with small amounts of Ti; Fe'' with Mn and Mg; Ca with Na and K. This confirms the formula of Palache & Gonyer and disproves that of Gossner & Mussgnug (1928), namely $4[Si_2O_6Ca\ Fe \cdot SiO_2]$, which does not represent the number of atoms in the unit cell or their proportions, and omits essential constituents.

*Systematic relations.* In the systematic mineralogies babingtonite follows rhodonite in the so-called triclinic section of the pyroxene group. The two minerals have similar geometrical elements, which is surprising in view of their apparently dissimilar compositions. Structural studies have shown that the pyroxene group is naturally limited to those species that have the structure of diopside; and thus the triclinic section of the pyroxene group has become a discredited misnomer.

Recently babingtonite has been variously classified: Gossner (1928) regards babingtonite as related to anorthite and epididymite; Palache & Gonyer (1932) concluded that babingtonite belongs in no existing group; Berman (1937) places babingtonite in a group of "miscellaneous pyroxenoids."

From the existing structural data on the two species we find that their geometrical similarity actually expresses near equality of the absolute lattice parameters; and that the cell contents show a relation that would not be suspected from the empirical formulas. These relations appear when we take the structural cell of babingtonite, in the second setting of Gossner & Mussgnug (1928, p. 279), turn it 180° about the vertical axis, and compare the resulting lattice parameters with those given for rhodonite by Gossner & Brückl (1928). Appending the two cell contents, as given by the cell volumes and densities, we have the following comparison:

| BABINGTONITE | RHODONITE |
|---|---|
| $a_0=7.54,\ b_0=12.43,\ c_0=6.73$ | $a_0=7.77,\ b_0=12.45,\ c_0=6.74$ |
| $\alpha=86°12',\ \beta=93°51',\ \gamma=112°22'$ | $\alpha=85°10',\ \beta=94°04',\ \gamma=111°29'$ |
| $Fe_2'''Fe_2''Ca_4Si_{10}O_{28}(OH)_2$. | $(Mn,\ Fe,\ Ca)_{10}Si_{10}O_{30}$. |

Although the above lattice parameters do not correspond to the normal setting, they do represent unit cells of the respective structural lattices; and since all unit cells of a simple lattice have the same volume the above comparison is valid. Such agreement in all of the six triclinic lattice parameters points to a close structural similarity in the two species. If we express the two cell contents as 10 $RSiO_3$, then babingtonite appears to have a rhodonite structure, with two oxygen positions occupied by hydroxyl and two cation positions unoccupied. Since the powder photographs of the two minerals, illustrated in figure 7, do not apparently show such close structural similarity, the above argument can only be tentatively accepted. An investigation of rhodonite must be made, similar to that presented in this paper, before the validity of our argument can be admitted.

Rhodonite and babingtonite show only a partial relation to the triclinic wollastonite group of Peacock (1935), whose general cell content is 6 $RSiO_3$. Without entering into details it may be said that the structural relation between rhodonite and wollastonite is confined to near equality of two of the principal lattice periods and the included axial angle; the remaining lattice parameters are quite dissimilar. This points to a similarity only in the ground plan of the two structures. We conclude therefore, that babingtonite should accompany rhodonite in one group of the pyroxenoids of Berman, while the wollastonite group forms another group in the same family.

*Summary.* Excellent crystals of babingtonite from Woburn, Massachusetts, are triclinic: $a:b:c=0.6417:1:0.5746$; $\alpha=91°31'$, $\beta=93°51'$, $\gamma=104°04'$ (Dauber's elements computed to the normal setting of Peacock). Fourteen known forms were observed; also the new forms $j\{310\}$, $e\{111\}$, $k\{121\}$, and the new but uncertain forms $\{350\}$, $\{121\}$. $X$-ray measurements, independent of the external geometry, gave: $a_0=7.39$ Å, $b_0=11.52$ Å, $c_0=6.61$ Å; $\alpha=91°48'$, $\beta=93°48'$, $\gamma=103°54'$; $a_0:b_0:c_0=0.642:1:0.574$. The agreement shows that the structural lattice was correctly inferred from the morphology. From existing analyses and densities the unit cell contains: $Fe_2'''Fe_2''Ca_4Si_{10}O_{28}(OH)_2$. New optical data:

| | $\phi$ | $\rho$ | $n$(Na) | | |
|---|---|---|---|---|---|
| $X$ (dark green) | −104° | 46° | 1.720 | ±0.003 | Positive |
| $Y$ (lilac) | 145 | 70 | 1.731 | | $2V=76°\pm2°$ |
| $Z$ (brown) | 39 | 51 | 1.753 | | $r>v$ strong |

Babingtonite and rhodonite form a group of structurally related pyroxenoids, which shows only partial relations to the wollastonite group.

*Acknowledgment.* The writer is under special obligation to Dr. Martin A. Peacock of Harvard University for invaluable aid in the preparation of this manuscript, and to Dr. Harry Berman for help in the $x$-ray determination.

## Explanation of the Figures

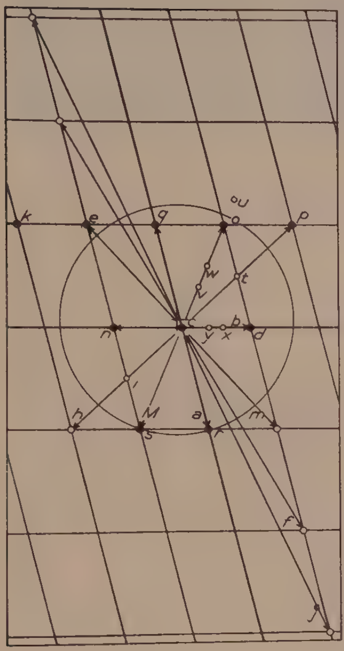
Fig. 1. Babingtonite: gnomonic projection of the known forms.

Fig. 2. Babingtonite: typical doubly terminated crystal from Woburn, Mass.

Figs. 3, 4. Babingtonite: relation of Dauber's setting to the normal setting, in the gnomonic projection and direct lattice; dotted cells and underlined symbols are those of Dauber.

Fig. 5. Babingtonite: relation of two unit cells of babingtonite in the normal setting (full lines and unprimed elements) and one unit cell of Gossner & Mussgnug (dotted lines and primed elements).

Fig. 6. Babingtonite: stereographic projection of the optical orientation and the positions of the optic axes.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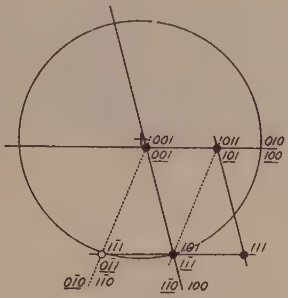
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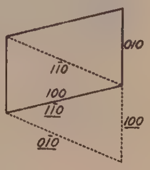
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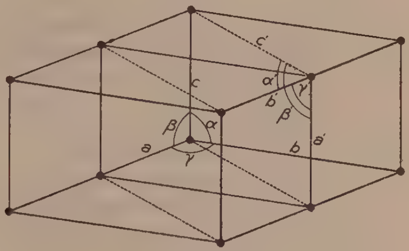
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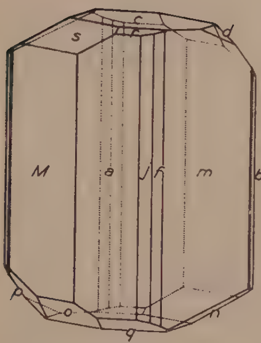
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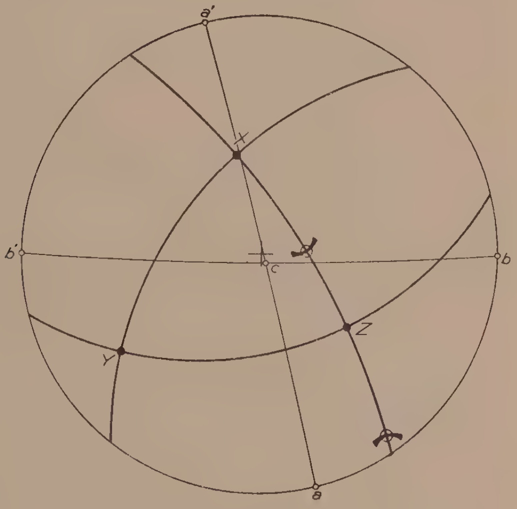
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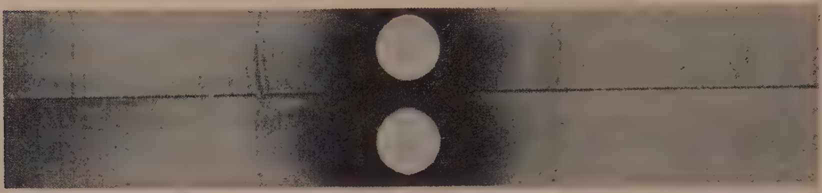

Fig. 7. Babingtonite: powder photographs of babingtonite (above) and rhodonite (below) taken with unfiltered iron radiation.

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# SPHALERITE FROM A PEGMATITE NEAR SPRUCE PINE, NORTH CAROLINA*

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A peculiar black sphalerite from the McKinney mine, near Spruce Pine, North Carolina, was brought to my attention in the summer of 1933 by Mr. B. C. Burgess, of Spruce Pine. The genetic relations of this sphalerite to the typical pegmatite minerals with which it is associated, are shown so clearly that the occurrence evoked unusual interest; and the locality was visited in 1934 and again in 1936. By 1934 the original sphalerite-bearing lens and a smaller one encountered later had been completely removed, but some tons were still on the waste dumps, and abundant material was secured for study. The McKinney mine is operated by open pit, and is one of the largest feldspar producers in the Spruce Pine district. It lies about 5 miles southwest of Spruce Pine, 3 miles northwest of Little Switzerland, and in the northeast quarter of the Mt. Mitchell geologic folio.

The dominant minerals of the pegmatite are microcline, plagioclase that varies from albite to oligoclase, quartz, muscovite, and a little garnet. Thus, except for the locally abundant sulphides, the minerals are those characteristic of pegmatites of the region. Sphalerite is by far the most abundant sulphide mineral, but chalcopyrite, pyrite, pyrrhotite, galena, covellite, scheelite, and a few alteration products are also present. The pegmatite also contains euxenite?, samarskite, and columbite as rare but conspicuous masses. Water-bearing joint planes have yielded very beautiful specimens of fluorescent hyalite which have found their way into many museums.

The sphalerite-bearing lens was several feet thick and is said to have extended almost across the pegmatite body, for a distance of perhaps a hundred feet or more. This great mass composed as it was of intergrown black sphalerite and white albite, must have been a spectacular mineralogical exhibit, since even individual specimens show striking contrasts.

The relations of the feldspars are well shown in a quarry opening to the south of the large quarry, where large rounded masses of microcline are enclosed in the replacing plagioclase. A contact between albite and microcline is shown in fig. 3, where it is marked by the narrow, irregular white area lying between sphalerite above and microcline (gray) below. Microscopic examination shows albite with small, complex interfingering masses penetrating the microcline. Where replacement has been complete the individual grains of albite (*Ab* 95 where associated with the sphalerite) vary from a small fraction up to several millimeters in great-

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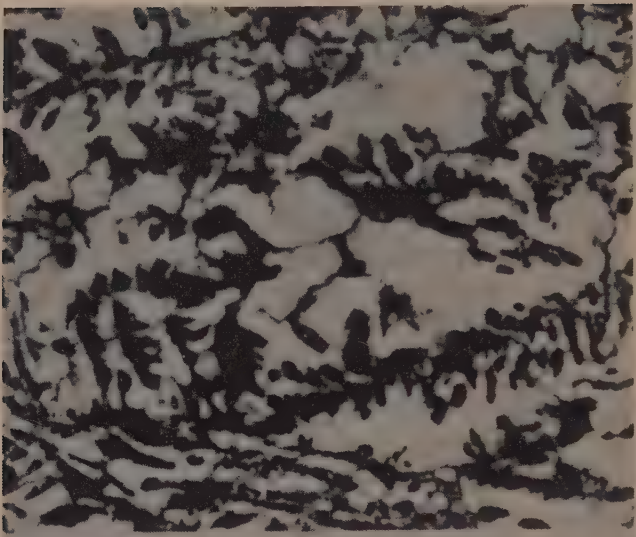

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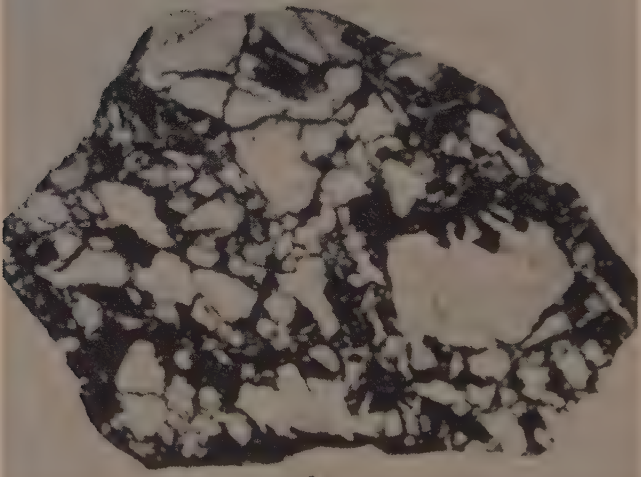

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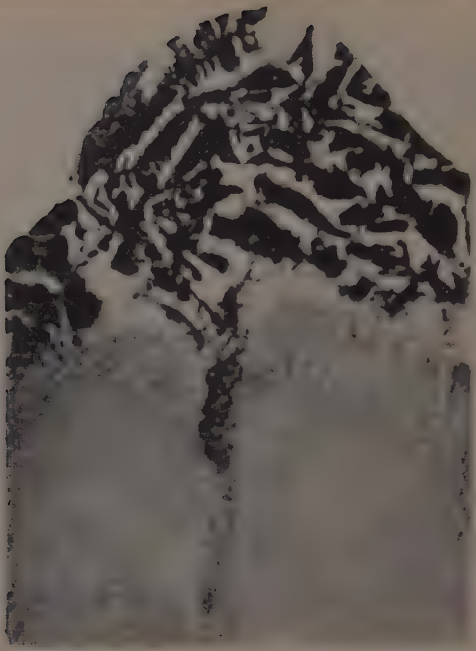
FIG. 1. Polished specimen illustrating the typical relations between albite and replacing sphalerite. Note the coarsely dendritic habit of the sphalerite. Natural size.

FIG. 2. Polished specimen illustrating fracturing of albite, and veinlets of sphalerite in albite (upper part of figure). Near the right side are spearhead-like areas of sphalerite which have replaced albite. Natural size.

est dimensions, and these interfinger in a very complex manner. Many of the larger albite areas are made up of small segments which give undulatory extinction as in badly strained quartz, and others are so warped that the cleavage planes are strongly curved. Associated with the secondary albite, or on the contact between albite and microcline are sporadic masses of muscovite which reach 20 to 30 centimeters in diameter. A microscopic study reveals numerous vein-like areas of muscovite, and other widely separated but uniformly oriented areas which interfinger with the albite. Some of these have warped or twisted forms that indicate distortion at the time the feldspars were locally fractured. Quartz forms irregular grains associated with albite, and veins up to several centimeters in diameter cut both microcline and albite.

The sphalerite-bearing lens was made up of about equal proportions of albite and sphalerite by volume, with only a small proportion of other minerals. In most of the material from this lens, sphalerite and albite are almost completely unaltered. The complexly intergrown habit of albite and sphalerite, which gives a coarsely dendritic structure, is shown in figs. 1 and 3. Many of the edges of the sphalerite are straight, others are irregular, and cusp-shaped or spearhead-like areas are characteristic. Rounded masses are conspicuously absent. Such structures have at times been assumed to indicate simultaneous crystallization, but it is known that replacement produces the same type of structures. The abundant veinlets of sphalerite that cut fractured albite, illustrated in fig. 2 and more rarely in fig. 1, show clearly that the sphalerite formed after the albite. Moreover, close inspection shows that sphalerite is invariably the invading mineral. The sphalerite in veinlets is identical in character with that in dendritic masses, and single crystal areas are commonly continuous from veins out into dendritic areas. The invasion of microcline by sphalerite along a quartz vein is shown in fig. 3, and veinlets of chalcopyrite in cleavages of microcline are shown in fig. 5. Figure 6 shows irregular areas of chalcopyrite which have partly replaced microcline. The partial replacement of quartz by sphalerite is shown in fig. 3, and microscopic study reveals numerous microscopic veinlets which are in part quartz and the rest sphalerite. In these the quartz occupies clean-cut fractures, but the sphalerite sends out numerous lateral invading areas into the microcline. The invasion of muscovite by sphalerite is illustrated in fig. 4, where sphalerite has developed in the cleavage planes of the mica. Garnet associated with sphalerite is commonly crushed, with sphalerite veinlets in the fractures.

Local areas that evidently came from the border of the sulphide lens, present very interesting mineral relations, although in quantity they are quite unimportant. In the hand specimens such areas show a larger



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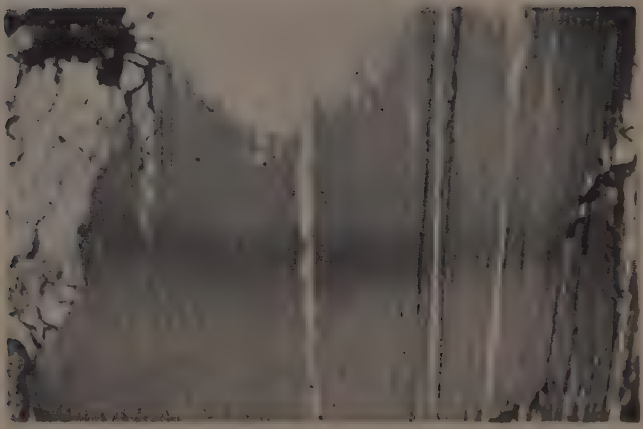

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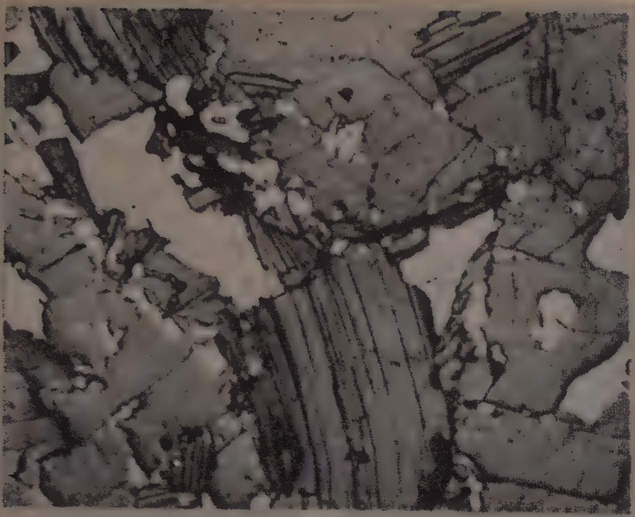
FIG. 3. Polished specimen illustrating the relations of albite-sphalerite to microcline. The lower half of the figure represents microcline cut by a vein of quartz. The narrow light-colored zone between microcline and sphalerite represents granular albite that has partly replaced microcline. Near the center sphalerite has replaced part of the quartz vein. 1/4 natural size.

FIG. 4. Polished specimen illustrating the formation of sphalerite (white vertical veins) in the cleavage planes of muscovite. Near the top is an area of albite (white), and on the left margin is intergrown sphalerite and albite. Reflected light. ×8.



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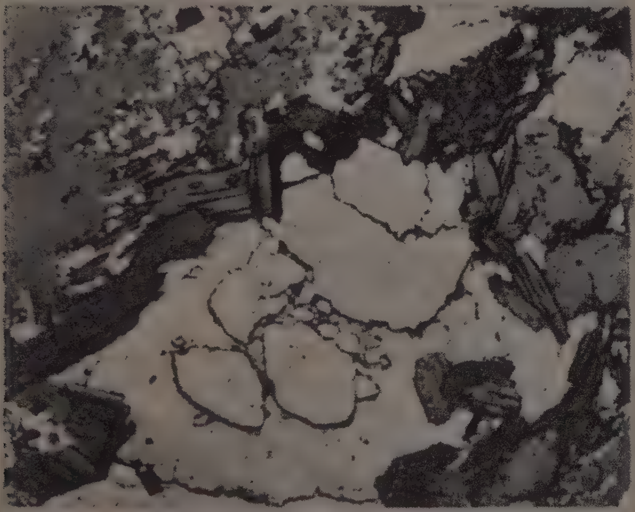

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FIG. 5. Polished specimen illustrating the relations of chalcopyrite. Gray areas with conspicuous cleavage are muscovite, and other gray areas are microcline. White is chalcopyrite. Lower left part of the figure shows chalcopyrite in a cleavage plane in microcline. Reflected light. ×8.

FIG. 6. Polished specimen illustrating the relations of pyrite and chalcopyrite. Near the center of the figure angular grains of pyrite are enclosed in later chalcopyrite. In the upper left portion of the figure patchy areas of chalcopyrite are replacing an area of microcline. Polished specimen. ×8.

proportion of pyrite and chalcopyrite than the main mass, and just outside of the sulphide mass, a zone 1 to 2 centimeters wide in the feldspars has commonly been stained by limonite. In many specimens there has been partial solution of sulphides and masses 1 to 2 centimeters wide have become pitted with cavities 1 to 2 millimeters across. Microscopic study shows that in this border material the sphalerite is somewhat paler in color than the main mass. Some areas contain subhedral crystals of sphalerite which have been slightly rounded, and are surrounded by very narrow reaction rims which appear to have a metacolloidal structure. Others contain abundant pyrite in tiny disseminated blebs, and hematite has formed along cleavages in sphalerite. Scheelite, in euhedral crystals that reach a length of a millimeter, have been observed near the contact between sphalerite and albite in several thin sections. Another specimen from the same zone contains chlorite which seems to have directly replaced albite and muscovite without biotite as and intermediate stage.

The mineralization in these border areas might be interpreted as a slightly later episode than that which produced the main mass of sphalerite, but it seems more probable that it represents the outer zone of mineralization where the solutions had become attenuated, and somewhat cooler. Depletion in the less soluble elements left the solutions relatively richer in others, and so a slightly different mineral suite was deposited. Here scheelite, more abundant pyrite, chalcopyrite, and galena were deposited, and chlorite replaced earlier minerals. A later group of changes are probably to be attributed to supergene processes. During this stage sphalerite was pitted by partial solution, and the remainder seems to have been originally identical with the type characteristic of the lens, but was subsequently leached by the removal of a part of its iron. This released iron now occurs as hematite in the cleavage planes of sphalerite and as limonite in contiguous feldspar. The development of covellite and the formation of hyalite were the result of supergene changes.

A strongly radioactive mineral that has not been analysed, but which has the optical properties of euxenite, was collected at the McKinney mine in 1934. Associated with this were small amounts of chalcopyrite, pyrite, and galena, which seem to have formed about the same time as the enclosing euxenite. With this are minute stains of orange-yellow gummite. The genetic relations of columbite and samarskite were not observed.

The mineral relations described in the foregoing sections show that the hypogene paragenesis falls into three fairly distinct stages. Pegmatite mineralization was initiated by the introduction of primary microcline. The second stage consisted in the partial replacement of microcline by albite, muscovite, quartz, and garnet. During the third stage all the earlier minerals were invaded and partly replaced by pyrite, sphalerite, pyrrhotite, chalcopyrite, galena, scheelite, and chlorite. Euxenite was probably introduced during the same period. There was no doubt a tendency for a mineral sequence within these groups, but they seem to have formed nearly together or overlapped so that the order within a group cannot be fully determined. It is probable that garnet followed the other minerals of its group.

Dr. M. N. Short has kindly studied the sulphides and the relations and has supplied the following descriptions of them:

"The hypogene minerals are pyrite, chalcopyrite, sphalerite, galena, and pyrrhotite. Pyrite is in part older (fig. 6), but all the others are essentially contemporaneous. Sphalerite is immensely more abundant than any other sulphide. It is followed in abundance by chalcopyrite, which is dominant in a few local samples. The others occur only in minute amounts. In specimens where chalcopyrite predominates, sphalerite occurs in chalcopyrite as small rounded, or irregular-shaped inclusions, not over a millimeter in diameter. These sphalerite grains in turn contain chalcopyrite in tiny rounded blebs irregularly dispersed through the host. Galena occurs as tiny rounded blebs in both chalcopyrite and sphalerite. Pyrrhotite occurs as tiny elongated or rounded blebs in sphalerite where it is associated with chalopyrite inclusions. Small amounts of covellite occur as a supergene alteration of chalcopyrite, where it forms aggregates of tiny plates at the boundaries between chalcopyrite and gangue minerals, and in cracks in chalcopyrite."

In the border material, sulphide deposition appears to have been a somewhat more protracted process than in the main mass. Here some of the pyrite is clearly older than sphalerite and part of the chalcopyrite is later. Scheelite and galena are not clearly dated. In some of the pale colored sphalerite, minute uniformly oriented and evenly distributed bleb-like areas of pyrite may be the result of exsolution. Hematite, limonite, covellite, gumite, and hyalite were the result of later supergene processes.

*Composition of sphalerite.* The following chemical analysis of the typical black sphalerite has been made by Mr. J. G. Fairchild.

Chemical Analysis of Sphalerite

| | |
|---|---|
| Zn | 59.34 |
| Fe | 6.16 |
| Cd | 0.23 |
| Mn | 0.05 |
| Cu | None |
| Pb | None |
| S | 34.11 |
| Insol. | 0.27 |
| Total | 100.16 |
| Gravity | 4.070 |

The sphalerite is high in iron as it contains 6.16 of Fe or 9.68 per cent of FeS, and this is no doubt the cause of the very dark color of the sphalerite from the McKinney mine. It is perfectly black in grains only a few tenths of a millimeter in diameter, but gives a chocolate-colored streak.

Under the microscope the color of the sphalerite is ochraceous orange (Ridgway) when examined in white light and in grains about 0.05 millimeters thick. These are dark but entirely limpid, and without dust-like inclusions.

Sphalerite has previously been recognized in pegmatites, but never in such large masses, or where the relations were so well shown. Dr. W. T. Schaller of the U. S. Geological Survey reports[1] small masses (2 or 3 centimeters in diameter) of similar black sphalerite in a pegmatite in the Hottinger mine near Bedford, Virginia. Mr. Hugh Spence, of the Canadian Bureau of Mines, has sent me specimens of a dark colored sphalerite from a pegmatite in Dill Township, Sudbury District, Ontario. He states[2] that it occurs in a small chimney-like zone near the wall of the pegmatite, but observes that it may be connected with one of the later zinc veins that occur in the district. Edwin J. Over, Jr., reports[3] small amounts of a black sphalerite which occurs together with galena in association with fluoride minerals in a pegmatite that lies near the junction of the highway and South Cheyenne Creek on Mt. Rosa, Pikes Peak district, El Paso County, Colorado.

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[1,2,3] Personal communication.

# CRYSTALLOGRAPHY OF VALENTINITE ($Sb_2O_3$) AND ANDORITE(?) ($2PbS \cdot Ag_2S \cdot 3Sb_2S_3$) FROM OREGON*

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## Contents

Introduction . . . . . 651
Valentinite . . . . . 652
  Axial Ratio . . . . . 652
  Forms and Angles . . . . . 653
  Discussion of Prism Zone . . . . . 657
  Combinations . . . . . 661
Andorite(?) . . . . . 662

## INTRODUCTION

A set of ore specimens from the Ochoco mining district, Oregon, submitted for mineralogical study by G. F. Loughlin of the U. S. Geological Survey, showed a number of unusual minerals. Their occurrence is mentioned in a recent report by Gilluly, Reed, and Park (1933). The locality is Gold Hill (Howard district), Ochoco Creek area, northeastern part of Crook County, central Oregon. The matrix of the specimens submitted was largely carbonate; calcite, manganian dolomite with $\omega$ index $=1.690$–$1.693$, and calcian rhodochrosite with $\omega=1.783$.

One specimen contained a few hair-like metallic crystals, which break when bent, probably due to a basal cleavage. They are provisionally assigned to jamesonite and the following measurements were obtained on one of the thicker hair-like crystals.

Table 1. Measurements of Jamesonite

| Measured | Jamesonite |
|---|---|
| $(110):(\bar{1}10) = 101°51'$ | 101°21′ |
| $(1\bar{1}0):(\bar{1}\bar{1}0) = 98\ 33$ | 101 22 |
| $(110):(120) = 19\ 26$ | 19 17 |
| (110):(001) cleavage = 90°–92° | 90 00 |

A few of the hair-like crystals, however, were very flexible and could easily be bent double, showing the presence of a second hair-like mineral with no basal cleavage. The material seems to correspond to the mixture of "feather ore" previously called warrenite, which, however, is a mixture of jamesonite and zinckenite, as previously described by Schaller (1911).

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A single prismatic crystal of another mineral, provisionally referred to andorite and described in the following paper, was found on one specimen. Other minerals present are: aragonite, pyrite, tetrahedrite, and two other metallic minerals, one lead-gray and another prismatic dark reddish-black, which could not be identified on account of the paucity of material.

Apparently this locality might yield several of the rarer silver sulphosalts and anyone having access to the locality should make a careful search for well crystallized minerals of this character.

A number of small non-metallic crystals in one of the cavities of a specimen proved to be valentinite, antimony oxide, $Sb_2O_3$, and their goniometric measurements showed a large number of crystal forms, many of them new. They are described on the following pages.

## VALENTINITE

The optical properties and chemical reactions of these crystals are typically those of valentinite. The optical axial planes for red and blue light are normal to each other and the negative axial angle is small, with strong dispersion. The doubly terminated crystals are small, about a millimeter in length, and have no attraction as specimens. They would probably pass unnoticed unless one was making a detailed examination of the mineralogy of the material.

### Axial Ratio

The $a$-axis is calculated from the average measured $\phi$ angles of the prisms of the seven measured crystals. The measurements for $B\{340\}$ and $C\{450\}$ are omitted as they show much greater divergence from the calculated angles than do those of the other prisms. Likewise, those prisms whose $\phi$ angle is very large (greater than 81°) are also omitted as they are too close to $\{100\}$ to yield ratios of comparative value. The $c$-axis is calculated from the average measurements of the $\rho$ angle of the new side dome $T\{0.11.8\}$. The axial ratio so obtained is $a:b:c=0.3930:1:0.4350$.

This ratio is close to those recently given by other authors, as follows:

| | $a:b:c$ |
|---|---|
| Spencer (1907): | 0.3938:1:0.4344 |
| Ungemach[1] (1912): | 0.3928:1:0.4333 |
| Cesàro (1925): | 0.3952:1:0.4342 |
| Schaller: | 0.3930:1:0.4350 |

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[1] Ungemach gave the axial ratio as 0.3936:1:0.4339. According to a personal communication from Prof. Palache (June 9, 1936), Cesàro, in a note, calls attention to an error in these values. The correct ratio is: 0.3928:1:0.4333.

The average of these four values gives the axial ratio of valentinite as $a:b:c=0.3939:1:0.4339$.

## FORMS AND ANGLES

A total of 22 forms were found on the 7 crystals measured. These include the two pinacoids $a\{100\}$ and $b\{010\}$, nineteen prisms of which 15 are new for valentinite, and the new side dome $T\{0.11.8\}$.

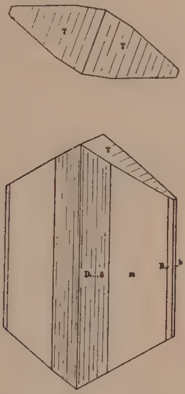

FIG. 1. Idealized drawing of valentinite from the Ochoco district, Crook County, Oregon. The crystal is about a millimeter high. Forms: $b\{010\}$, $m\{110\}$, $T\{0.11.8\}$. The narrow striated face $B$ adjoining $b\{010\}$, shows the position of $A\{350\}$, $B\{340\}$, and $C\{450\}$. The broad striated area in front includes the prisms from $D\{10.9.0\}$ to $S\{910\}$.

The general habit and distribution of forms on these crystals are shown in Figure 1. The dominant forms are $m\{110\}$ and the new side dome $T\{0.11.8\}$ which is the only terminal form present. The prisms other than $m\{110\}$ are all line faces. The side pinacoid $b\{010\}$ is generally narrow but wider than a line face whereas $a\{100\}$ is a line face. The faces of $m$ are vertically striated and those of $T\{0.11.8\}$ are horizontally striated parallel to their intersection. The reflections from the unit prisms were good; all the others were poor.

TABLE 2. VALENTINITE: FORMS AND ANGLES

New forms are starred

| Form | No. crystals | No. faces | Average measured $\phi$ angle | Calculated $\phi$ angle | Difference |
|---|---|---|---|---|---|
| b{010} | 7 | 10 | 0°09′ | 0°00′ | 0°09′ |
| a{100} | 2 | 2 | 89 42 | 90 00 | 18 |
| *A{350} | 3 | 3 | 56 48 | 56 43 | 05 |
| *B{340} | 2 | 2 | 62 44 | 62 18 | 26 |
| *C{450} | 3 | 3 | 64 07 | 63 47 | 20 |
| m{110} | 7 | 28 | 68 39 | 68 30 | 09 |
| *D{10.9.0} | 5 | 8 | 70 36 | 70 29 | 07 |
| *E{760} | 4 | 7 | 71 26 | 71 21 | 05 |
| σ{540} | 5 | 7 | 72 33 | 72 31 | 02 |
| *F{430} | 5 | 9 | 73 35 | 73 33 | 02 |
| *G{10.7.0} | 4 | 6 | 74 32 | 74 35 | 03 |
| *H{14.9.0} | 6 | 8 | 75 48 | 75 48 | 00 |
| *J{530} | 4 | 5 | 76 45 | 76 42 | 03 |
| *K{950} | 4 | 5 | 77 48 | 77 40 | 08 |
| *μ{210} | 4 | 6 | 78 54 | 78 52 | 02 |
| *L{730} | 3 | 4 | 80 24 | 80 25 | 01 |
| *M{830} | 3 | 3 | 81 41 | 81 36 | 05 |
| *π{310} | 3 | 4 | 82 42 | 82 31 | 11 |
| *N{410} | 3 | 4 | 84 22 | 84 23 | 01 |
| *P{510} | 3 | 3 | 85 47 | 85 30 | 17 |
| *S{910} | 3 | 3 | 87 35 | 87 30 | 05 |
| *T{0.11.8} | 7 | 7 | 30 53[a] | 30 49[a] | 04 |

[a] The $\rho$ angle.

TABLE 3. VALENTINITE: MEASUREMENTS OF $\phi$ ANGLE OF m{110}

| Crystal no. | Limits | Average of fair and good reflections |
|---|---|---|
| 1 | 68°03′–68°25′ | 68°23′ |
| 2 | 68 32 –68 41 | 68 36 |
| 3 | 68 43 –69 03 | 68 46 |
| 4 | 68 38 –69 30 | 68 55 |
| 5 | 68 26 –68 46 | 68 37 |
| 6 | 68 34 –68 46 | 68 40 |
| 7 | 68 01 –68 38 | 68 37 |

Average = 68°39′

TABLE 4. VALENTINITE: MEASUREMENTS OF $\phi$ ANGLE OF OTHER PRISMS

| | *A*{350} | *B*{340} | *C*{450} | *D*{10.9.0} | *E*{760} |
|---|---|---|---|---|---|
| Calculated | 56°43′ | 62°18′ | 63°47′ | 70°29′ | 71°21′ |
| Average of measurements | 56 48 | 62 44 | 64 07 | 70 36 | 71 26 |
| Individual measurements | 2— 56 13 | 5— 62 45 | 1— 63 45 | 3— 70 37 | 3— 71 36 |
| | 4— 57 31 | 6— 62 37 | 6— 64 18 | 3— 70 47 | 4— 71 25 |
| | 5— 56 39 | | 7— 64 18 | 4— 70 34 | 4— 71 35 |
| | | | | 5— 70 49 | 5— 71 46 |
| | | | | 6— 70 15 | 5— 71 25 |
| | | | | 6— 70 51 | 5— 71 03 |
| | | | | 7— 70 47 | 6— 71 15 |
| | | | | 7— 70 11 | |
| | $\sigma${540} | *F*{430} | *G*{10.7.0} | *H*{14.9.0} | *J*{530} |
| Calculated | 72°31′ | 73°33′ | 74°35′ | 75°48′ | 76 42′ |
| Average of measurements | 72 33 | 73 35 | 74 32 | 75 48 | 76 45 |
| Individual measurements | 2— 72 27 | 1— 73 29 | 2— 74 25 | 1— 76 09 | 2— 76 21 |
| | 2— 72 30 | 2— 73 50 | 2— 74 45 | 2— 75 28 | 2— 76 51 |
| | 3— 72 30 | 2— 73 37 | 2— 74 23 | 2— 75 36 | 3— 76 39 |
| | 3— 72 20 | 2— 73 51 | 3— 74 42 | 4— 75 51 | 5— 77 17 |
| | | 3— 73 26 | | 5— 75 59 | |
| | 4— 72 57 | | 5— 74 27 | | 6— 76 35 |
| | | 3— 73 26 | | 6— 75 48 | |
| | | 5— 73 23 | | | |
| | 6— 72 18 | | 6— 74 31 | 6— 76 10 | |
| | | 5— 73 26 | | | |
| | 7— 72 52 | 6— 73 51 | | 7— 75 20 | |
| | *K*{950} | $\mu${210} | *L*{730} | *M*{830} | $\pi${310} |
| Calculated | 77°40′ | 78°52′ | 80°25′ | 81°36′ | 82°31′ |
| Average of measurements | 77 48 | 78 54 | 80 24 | 81 41 | 82 42 |
| Individual measurements | 1— 77 42 | 2— 78 36 | 3— 80 06 | 1— 81 36 | 1— 82 29 |
| | 3— 77 44 | 2— 78 53 | 4— 80 42 | 2— 81 49 | 4— 82 07 |
| | 5— 77 25 | 3— 79 04 | 4— 80 42 | 4— 81 39 | 6— 82 55 |
| | 5— 77 59 | 4— 79 10 | 5— 80 07 | | 6— 83 17 |
| | 6— 78 11 | 5— 78 24 | | | |
| | | 5— 79 18 | | | |

| | *N*{410} | *P*{510} | *S*{910} | | |
|---|---|---|---|---|---|
| Calculated | 84°23′ | 85°30′ | 87°30′ | | |
| Average of measurements | 84 22 | 85 47 | 87 35 | | |
| Individual measurements | 3— 83 54 | 2— 85 59 | 4— 87 39 | | |
| | 4— 84 52 | 4— 85 58 | 5— 87 24 | | |
| | 5— 84 19 | 5— 85 24 | 7— 87 43 | | |
| | 5— 84 23 | | | | |

TABLE 5. VALENTINITE: MEASUREMENTS OF *T*{0.11.8}

| Crystal no. | Measured | | Difference from calculated $\rho$ angle | |
|---|---|---|---|---|
| | $\phi$ | $\rho$ | {0.11.8} | {043} |
| 1 | 0°56′ | 31°48′ | 0°59′ | 1°45′ |
| 2 | — | 32 | — | — |
| 2 | — | 31 | — | — |
| 3 | 0 42 | 30 42 | 07 | 39 |
| 3 | 0 11 | 30 53 | 04 | 50 |
| 4 | 0 34 | 31 12 | 23 | 1 09 |
| 4 | 0 34 | 31 09 | 20 | 1 06 |
| 5 | 0 52 | 31 01 | 12 | 58 |
| 5 | 0 23 | 30 23 | 26 | 20 |
| 6 | 0 10 | 30 51 | 02 | 48 |
| 6 | 0 10 | 30 52 | 03 | 49 |
| 7 | 0 39 | 30 15 | 34 | 12 |
| 7 | 0 39 | 30 36 | 13 | 33 |

Average (omitting crystal no. 2) = 30°53′.
Calculated = 30 49 .

The indices {0.11.8} seem to be the simplest which can be given to this new side dome. The calculated $\rho$ angles for other indices, close to {0.11.8}, are as follows:

$\rho$
{065} = 27°30′
{043} = 30 03
{0.11.8} = 30 49
{075} = 31 17
{032} = 33 04
Average of measured angles = 30°53′

The closest calculated angle for a simple form is that for {043} a form not listed for valentinite, but not a single one of the 13 measurements is as low as 30°03′ though two measurements approach this value. As the last column in the preceding table shows, the differences between the measured angles and 30°03′ are considerable. The differences between the average measured angle for *T* and the nearest known forms, {065} and {032}, are also considerable.

Difference from {065} = 3°23′
Difference from {032} = 2 11

A discussion of the side dome series of forms from (001) to (010) does not help in deciding the correct indices for *T*. Taking the zone segment from (011) to (021), in the middle of which *T* lies, and reducing it to the general type $0 \cdots \infty$, *T* becomes $\frac{3}{7}$ instead of the normal $\frac{1}{2}$. The form {043} would yield $\frac{1}{2}$ but as just shown the measurements do not agree with these indices.

| | *i* | — | *Q* | *T* | *g* | *f* | *X* |
|---|---|---|---|---|---|---|---|
| | 011 | 098 | 065 | 0.11.8 | 032 | 053 | 021 |
| | 1 | $\frac{9}{8}$ | $\frac{6}{5}$ | $\frac{11}{8}$ | $\frac{3}{2}$ | $\frac{5}{3}$ | 2 |
| $\frac{v-v_1}{v_2-v}=$ | 0 | $\frac{1}{7}$ | $\frac{1}{4}$ | $\frac{3}{7}$ | 1 | 2 | $\infty$ |
| $N_2=$ | 0 | $\left(\frac{1}{7}\right)$ | $\left(\frac{1}{4}\right)$ | $\left[\frac{3}{7}\right]$ | 1 | 2 | $\infty$ |

## DISCUSSION OF PRISM ZONE

The following discussion of the prism zone follows the well known method of Goldschmidt's comparison with normal series. It not only served to confirm the correctness of the indices of many of the new prisms but it has been of greatest value in deciding the correct indices of three of the new prisms with more complex indices.

The poor reflections obtained from most of these new prisms with a consequent considerable variation in the measured angles do not suffice, alone, to correctly determine the indices.

Including the two pinacoids *b*{010} and *a*{100} there are now 26 forms in this zone, including the two given by Cesàro (1925). This zone consists naturally of two sections extending from *b*{010} to *m*{110} and from *m*{110} to *a*{100}. In the first section from *b* to *m*, the $\phi$ angles of the forms differ from adjacent ones by many degrees except for the two forms *B*{340} and *C*{450}, where the difference is only 1°29′. But for the second section from *m* to *a*, the forms are closely crowded together and are about one degree apart.

The first section is:

| | $b$ | $\rho$ | $x$ | $n$ | $A$ | $B$ | $C$ | $m$ |
|---|---|---|---|---|---|---|---|---|
| | 010 | 160 | 130 | 120 | 350 | 340 | 450 | 110 |
| $\frac{h}{k}=$ | 0 | $\frac{1}{6}$ | $\frac{1}{3}$ | $\frac{1}{2}$ | $\frac{3}{5}$ | $\frac{3}{4}$ | $\frac{4}{5}$ | 1 |
| $\frac{v}{1-v}=$ | 0 | $\frac{1}{5}$ | $\frac{1}{2}$ | 1 | $\frac{3}{2}$ | 3 | 4 | $\infty$ |
| $N_3=$ | 0 | $\left(\frac{1}{5}\right)$ | $\frac{1}{2}$ | 1 | $\frac{3}{2}$ | 3 | (4) | $\infty$ |

The two forms $\rho\{160\}$ and $C\{450\}$ are extra. Splitting the zone at $n\{120\}$:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0 | $\frac{1}{6}$ | $\frac{1}{3}$ | $\frac{1}{2}$ | | $\frac{1}{2}$ | $\frac{3}{5}$ | $\frac{3}{4}$ | $\frac{4}{5}$ | 1 |
| $2v=$ | 0 | $\frac{1}{3}$ | $\frac{2}{3}$ | 1 | $\frac{v-v_1}{v_2-v}=$ | 0 | $\frac{1}{4}$ | 1 | $\frac{3}{2}$ | $\infty$ |
| $\frac{v}{1-v}=$ | 0 | $\frac{1}{2}$ | 2 | $\infty$ | $2v=$ | 0 | $\frac{1}{2}$ | 2 | 3 | $\infty$ |
| $N_2=$ | 0 | $\frac{1}{2}$ | 2 | $\infty$ | $N_3=$ | 0 | $\frac{1}{2}$ | 2 | 3 | $\infty$ |

All the forms in this section can be transferred to parts of the normal series.

The second section, from $m\{110\}$ to $a\{100\}$ is a long one with 19 forms and runs continuously with no well defined break. The form with the simplest indices, except for the two end members $m\{110\}$ and $a\{100\}$ is $\mu\{210\}$ which moreover lies in the middle of the zone. This zone is therefore split into two sections at $\mu\{210\}$, which are considered separately.

The first section from $m$ to $\mu$ gives:

| | $m$ | $D$ | $E$ | $\sigma$ | $F$ | $G$ | $H$ | $J$ | $K$ | $\mu$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | 110 | 10.9.0 | 760 | 540 | 430 | 10.7.0 | 14.9.0 | 530 | 950 | 210 |
| $\frac{h}{k}=$ | 1 | $\frac{10}{9}$ | $\frac{7}{6}$ | $\frac{5}{4}$ | $\frac{4}{3}$ | $\frac{10}{7}$ | $\frac{14}{9}$ | $\frac{5}{3}$ | $\frac{9}{5}$ | 2 |
| $v-1=$ | 0 | $\frac{1}{9}$ | $\frac{1}{6}$ | $\frac{1}{4}$ | $\frac{1}{3}$ | $\frac{3}{7}$ | $\frac{5}{9}$ | $\frac{2}{3}$ | $\frac{4}{5}$ | 1 |
| $\frac{v}{1-v}=$ | 0 | $\frac{1}{8}$ | $\frac{1}{5}$ | $\frac{1}{3}$ | $\frac{1}{2}$ | $\frac{3}{4}$ | $\frac{5}{4}$ | 2 | 4 | $\infty$ |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $2v=$ | 0 | $\frac{1}{4}$ | $\frac{2}{5}$ | $\frac{2}{3}$ | 1 | $\frac{3}{2}$ | $\frac{5}{2}$ | 4 | 8 | ∞ |
| $N_4=$ | 0 | $\frac{1}{4}$ · | $\frac{2}{5}$ · · | $\frac{2}{3}$ · | 1 · | $\frac{3}{2}$ · | $\frac{5}{2}$ · · | 4 | (8) | ∞ |

All the forms agree with the normal series $N_4$ except for (8), equivalent to $K\{950\}$, which is extra.

If this zone section be further split at 1, equivalent to $F\{430\}$, the two sections will agree with $N_3$.

| | *m* | *D* | *E* | *σ* | *F* |
|---|---|---|---|---|---|
| | 0 | $\frac{1}{4}$ | $\frac{2}{5}$ | $\frac{2}{3}$ | 1 |
| $\frac{v}{1-v}=$ | 0 | $\frac{1}{3}$ | $\frac{2}{3}$ | 2 | ∞ |
| $N_3=$ | 0 | $\frac{1}{3}$ · | $\frac{2}{3}$ · · | 2 · | ∞ |

| | *F* | *G* | *H* | *J* | *K* | *μ* |
|---|---|---|---|---|---|---|
| | 1 | $\frac{3}{2}$ | $\frac{5}{2}$ | 4 | 8 | ∞ |
| $v-1=$ | 0 | $\frac{1}{2}$ | $\frac{3}{2}$ | 3 | 7 | ∞ |
| $N_3=$ | 0 · | $\frac{1}{2}$ · · | $\frac{3}{2}$ · | 3 | (7) | ∞ |

For the form $D\{10.9.0\}$ the measurements alone would hardly differentiate between $\{11.10.0\}$, $\{10.9.0\}$, and $\{980\}$ as the following comparison shows.

| | | $\phi$ |
|---|---|---|
| *D*, average measured | | 70°36′ |
| Calculated for | {11.10.0} | 70 18 |
| | {10.9.0} | 70 29 |
| | {980} | 70 42 |

Of the eight measurements of *D*, two agree better with {11.10.0}, one better with {10.9.0}, four better with {980}, while one is half way between {10.9.0} and {980}. But the discussion shows that {10.9.0} is the correct symbol.

In the discussion {11.10.0} would yield $\frac{2}{9}$ and {980} would yield $\frac{2}{7}$ in the normal series $N_4$ instead of $\frac{1}{4}$, and {11.10.0} would yield $\frac{2}{7}$ and {980} would yield $\frac{2}{5}$ in the normal series of $N_3$ instead of $\frac{1}{3}$.

For the complex indices of *G*, namely {10.7.0} the question might arise whether the simpler ones {750} might not be better. The comparison of measured and calculated angles shows:

| | $\phi$ |
|---|---|
| *G*, average measured | 74°32′ |
| Calculated for {10.7.0} | 74 35 |
| Calculated for {750} | 74 17 |

Of the six faces of *G* measured, the angles are closer to {750} for only two of the measurements. The discussion would yield $\frac{4}{3}$ instead of $\frac{3}{2}$ for $N_4$, and $\frac{1}{3}$ instead of $\frac{1}{2}$ for $N_3$. The discussion therefore verifies the measurements that the more complex indices {10.7.0} are to be preferred for the correct indices of *G*.

The most complicated indices of all the new forms here described are those of *H*{14.9.0}. The discussion shows however that these indices readily fall into the normal series. Simpler indices which suggest themselves are {320}, {850}, and {11.7.0}. The comparison of measured and calculated angles is as follows.

| | $\phi$ |
|---|---|
| *H*, average measured | 75°48′ |
| Calculated for {850} | 76 10 |
| {11.7.0} | 76 56 |
| {14.9.0} | 75 47 |
| {320} | 75 17 |

Of the eight measured faces of *H*, one (75°20′) agrees very closely with the calculated value for {320}; two agree very closely with the calculated value for {850}, and two agree closely with the calculated value for {11.7.0}. As all the reflections measured were poor, there is no justification for claiming that the measurements show four distinct forms instead of one. The only question is as to the correct indices of this form. And according to the measurements, the only question is between {14.9.0} and {11.7.0}. The measurements alone are not sufficient to decide this question as the following comparison shows. The differences (Δ) between the measurements and the calculated angles for {14.9.0} and {11.7.0} are as follows:

| Crystal no. | Measurements | Δ{14.9.0} | Δ{11.7.0} |
|---|---|---|---|
| 1 | 76°09′ | +21′ | +13′ |
| 2 | 75 28 | −20 | −28 |
| 2 | 75 36 | −12 | −20 |
| 4 | 75 51 | +03 | −05 |
| 5 | 75 59 | +11 | +03 |
| 6 | 75 48 | 0 | −08 |
| 6 | 76 10 | +22 | +14 |
| 7 | 75 20 | −28 | −36 |

There is practically no choice, the measurements agreeing about as well with one as with the other.

The discussion however shows that {11.7.0} reduces to $\frac{8}{3}$ for $N_4$. This value of $\frac{8}{3}$ does not belong in the normal series $N_4$ and moreover is more complicated than $\frac{5}{2}$, derived from {14.9.0}, which does belong in $N_4$. In the normal series $N_3$, {11.7.0} becomes $\frac{5}{3}$ which does not belong in $N_3$ and is more complex than $\frac{3}{2}$ derived from {14.9.0}, which does belong in $N_3$.

The discussion therefore shows that the correct indices for *H* are {14.9.0}, a fact which cannot be determined from the measurements alone.

Although the form *K*{950} is extra in both $N_4$ and $N_3$, it causes no disturbance in the normal series and the measurements of the five faces of *K*, three of which agree closely with the calculated value, fully substantiate this form.

The second section of the zone, from $\mu${210} to *a*{100}, is as follows:

| | $\mu$ | $L$ | $M$ | $\pi$ | — | $R$ | $N$ | $P$ | $S$ | $a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | 210 | 730 | 830 | 310 | 17.5.0 | 720 | 410 | 510 | 910 | 100 |
| $\frac{h}{k}=$ | 2 | $\frac{7}{3}$ | $\frac{8}{3}$ | 3 | $\frac{17}{5}$ | $\frac{7}{2}$ | 4 | 5 | 9 | $\infty$ |
| $\frac{v}{2}=$ | 1 | $\frac{7}{6}$ | $\frac{4}{3}$ | $\frac{3}{2}$ | $\frac{17}{10}$ | $\frac{7}{4}$ | 2 | $\frac{5}{2}$ | $\frac{9}{2}$ | $\infty$ |
| $v-1=$ | 0 | $\frac{1}{6}$ | $\frac{1}{3}$ | $\frac{1}{2}$ | $\frac{7}{10}$ | $\frac{3}{4}$ | 1 | $\frac{3}{2}$ | $\frac{\ }{2}$ | $\infty$ |
| $2v=$ | 0 | $\frac{1}{3}$ | $\frac{2}{3}$ | 1 | $\frac{7}{5}$ | $\frac{3}{2}$ | 2 | 3 | 7 | $\infty$ |
| $N_3=$ | 0 | $\frac{1}{3}$ | $\frac{2}{3}$ | 1 | $\left(\frac{7}{5}\right)$ | $\frac{3}{2}$ | 2 | 3 | (7) | $\infty$ |

This section of the zone gives nearly a perfect normal $N_3$ series, with only one member ($\frac{1}{2}$) missing and two extras. The form {720} of Cesàro, to which the letter *R* is assigned, fits in perfectly. The form {17.5.0} is undoubtedly vicinal to {720}, Cesàro giving a calculated difference of only 0°11′.

The form *S*{910} is extra in the normal series but is well substantiated by the measurements of three faces.

## COMBINATIONS

The combinations observed on the seven measured crystals of valentinite are shown in the following table.

TABLE 6. VALENTINITE: COMBINATIONS OBSERVED ON THE SEVEN MEASURED CRYSTALS

| Form | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| *b*{010} | *b* | *b* | *b* | *b* | *b* | *b* | *b* |
| *a*{100} | *a* | — | — | *a* | — | — | — |
| *A*{350} | — | *A* | — | *A* | *A* | — | — |
| *B*{340} | — | — | — | — | *B* | *B* | — |
| *C*{450} | *C* | — | — | — | — | *C* | *C* |
| *m*{110} | *m* | *m* | *m* | *m* | *m* | *m* | *m* |
| *D*{10.9.0} | — | — | *D* | *D* | *D* | *D* | *D* |
| *E*{760} | — | — | *E* | *E* | *E* | *E* | — |
| *σ*{540} | — | *σ* | *σ* | *σ* | — | *σ* | *σ* |
| *F*{430} | *F* | *F* | *F* | — | *F* | *F* | — |
| *G*{10.7.0} | — | *G* | *G* | — | *G* | *G* | — |
| *H*{14.9.0} | *H* | *H* | — | *H* | *H* | *H* | *H* |
| *J*{530} | — | *J* | *J* | — | *J* | *J* | — |
| *K*{950} | *K* | — | *K* | — | *K* | *K* | — |
| *μ*{210} | — | *μ* | *μ* | *μ* | *μ* | — | — |
| *L*{730} | — | — | *L* | *L* | *L* | — | — |
| *M*{830} | *M* | *M* | — | *M* | — | — | — |
| *π*{310} | *π* | — | — | *π* | — | *π* | — |
| *N*{410} | — | — | *N* | *N* | *N* | — | — |
| *P*{510} | — | *P* | — | *P* | *P* | — | — |
| *S*{910} | — | — | — | *S* | *S* | — | *S* |
| *T*{0.11.8} | *T* | *T* | *T* | *T* | *T* | *T* | *T* |

## ANDORITE(?)

The single prismatic crystal referred to in the introduction to valentinite was about a millimeter long and of a dark gray to nearly black

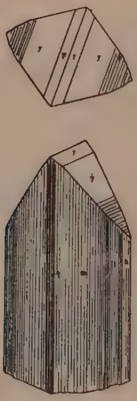

FIG. 2. Idealized drawing of crystal of andorite(?). Crystal about a millimeter high Forms: *k*{120}, *l*{230}, *m*{110}, *o*{320}, *y*{031}, *γ*{021}, *F*{052}.

color. It was detached and measured on the goniometer with the results shown below. The crystal was lost when it was attempted to apply microchemical tests.

A striated prism zone, terminated essentially only by side domes, giving poor reflections, made it impossible to decide whether the symmetry was orthorhombic or monoclinic. An extended comparison of the measured angles with those listed in the literature supplemented by a comparison of the habit with those of possible minerals, as given by Goldschmidt's *Atlas der Krystallformen*, lead to the conclusion that the measured crystal was either andorite, $2PbS \cdot Ag_2S \cdot 3Sb_2S_3$, or freieslebenite, $3PbS \cdot 2Ag_4S \cdot 2Sb_2S_3$, with a considerable preference for andorite.

A total of 40 faces were measured, of which about half could be correlated with 13 forms of andorite and with 15 forms of freieslebenite.

The faces measured are listed below in the order of measurement, with the corresponding forms and angles for andorite and for freieslebenite. No attempt was made to interpret the measurements of these prism faces (nos. 7, 9, 17, 23, 26, and 34) for which no agreement could be noted with the known forms of either andorite or freieslebenite.

The axial ratios used are, for andorite, $a:b:c = 0.6771:1:0.4458$, and for freieslebenite, $a:b:c = 0.5871:1:0.9277, \beta = 87°46'$.

TABLE 7. ANDORITE AND FREIESLEBENITE: COMPARISON OF MEASURED ANGLES

| No. | Note book letter | Measured | | Andorite | | | Freieslebenite | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | Form | $\phi$ | $\rho$ | Form | $\phi$ | $\rho$ |
| 1 | $a_1$ | 44°06′ | 90°00′ | 230 | 44°34′ | 90°00′ | 350 | 45°39′ | 90°00′ |
| 2 | $a$ | 45 22 | 90 00 | | | | | | |
| 3 | $b$ | 66 34 | 90 00 | 320 | 65 43 | 90 00 | 430 | 66 15 | 90 00 |
| 4 | $c$ | 85 22 | 90 00 | — | — | — | 810 | 85 48 | 90 00 |
| 5 | $d$ | 87 24 | 90 00 | 100 | 90 00 | 90 00 | 100 | 90 00 | 90 00 |
| 6 | $e$ | 82 20 | 90 00 | 510 | 82 18 | 90 00 | 510 | 83 18 | 90 00 |
| 7 | $f_1$ | 68 12 | 90 00 | — | — | — | — | — | — |
| 8 | $f_2$ | 66 04 | 90 00 | 320 | 65 43 | 90 00 | 430 | 66 15 | 90 00 |
| 9 | $f_3$ | 64 47 | 90 00 | — | — | — | — | — | — |
| 10 | $f_4$ | 63 07 | 90 00 | 430 | 63 05 | 90 00 | — | — | — |
| 11 | $f_5$ | 61 39 | 90 00 | — | — | — | 110 | 59 36 | 90 00 |
| 12 | $f_6$ | 54 17 | 90 00 | 110 | 55 54 | 90 00 | 560 | 54 51 | 90 00 |
| 13 | $f_7$ | 45 12 | 90 00 | 230 | 44 34 | 90 00 | 350 | 45 39 | 90 00 |
| 14 | $g$ | 36 54 | 90 00 | 120 | 36 27 | 90 00 | — | — | — |
| 15 | $g_1$ | 35 29 | 90 00 | — | — | — | 250 | 34 17 | 90 00 |
| 16 | $z$ | 36 36 | 90 00 | 120 | 36 27 | 90 00 | — | — | — |
| 17 | $y$ | 38 33 | 90 00 | — | — | — | — | — | — |
| 18 | $x$ | 40 37 | 90 00 | — | — | — | 120 | 40 26 | 90 00 |
| 19 | $w$ | 43 00 | 90 00 | 230 | 44 34 | 90 00 | — | — | — |

TABLE 7. (*Concluded*).

| No. | Note book letter | Measured | | Andorite | | | Freieslebenite | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | Form | $\phi$ | $\rho$ | Form | $\phi$ | $\rho$ |
| 20 | *v* | 46 11 | 90 00 | — | — | — | 350 | 45 39 | 90 00 |
| 21 | *u* | 53 59 | 90 00 | — | — | — | 450 | 53 45 | 90 00 |
| 22 | *t* | 56 08 | 90 00 | 110 | 55 54 | 90 00 | 560 | 54 51 | 90 00 |
| 23 | *s* | 57 04 | 90 00 | — | — | — | — | — | — |
| 24 | *r* | 58 17 | 90 00 | — | — | — | 110 | 59 36 | 90 00 |
| 25 | *q* | 63 12 | 90 00 | 430 | 63 05 | 90 00 | — | — | — |
| 26 | *p* | 68 12 | 90 00 | — | — | — | — | — | — |
| 27 | *o* | 70 20 | 90 00 | 210 | 71 18 | 90 00 | — | — | — |
| 28 | *n* | 66 33 | 90 00 | 320 | 65 43 | 90 00 | 430 | 66 15 | 90 00 |
| 29 | *m* | 64 03 | 90 00 | 430 | 63 05 | 90 00 | — | — | — |
| 30 | *l* | 57 05 | 90 00 | 110 | 55 54 | 90 00 | — | — | — |
| 31 | *k* | 54 22 | 90 00 | — | — | — | 560 | 54 51 | 90 00 |
| 32 | *j* | 44 49 | 90 00 | 230 | 44 34 | 90 00 | 350 | 45 39 | 90 00 |
| 33 | *i* | 36 32 | 90 00 | 120 | 36 27 | 90 00 | — | — | — |
| 34 | *h* | 37 15 | 90 00 | — | — | — | — | — | — |
| 35 | *B* | 0 19 | 52 23 | 031 | 0 00 | 53 13 | 032 | 1 36 | 54 18 |
| 36 | *D* | 0 19 | 52 27 | 031 | 0 00 | 53 13 | 032 | 1 36 | 54 18 |
| 37 | *C* | 0 19 | 47 07 | 052 | 0 00 | 48 06 | 054 | 1 55 | 49 14 |
| 38 | *E* | 2 55 | 38 20 | 021 | 0 00 | 41 43 | 011 | 2 24 | 42 52 |
| | | | | | | | 034 | 3 12 | 34 52 |
| 39 | $E_1$ | 75 51 | 41 08 | 524[a] | 74 51 | 41 07 | 214[b] | 74 21 | 40 41 |
| | | | | 312 | 77 17 | 45 21 | | | |
| 40 | *F* | 19 31 | 60 09 | 141[a] | 20 16 | 62 15 | 153[b] | 19 54 | 62 22 |

[a] Form not known for andorite.

[b] Form not known for freieslebenite.

Faces number 39 and 40 are extremely minute; they appear as mere bright specks on the goniometer but gave distinct though poor reflections. The measurements agree fairly well with the calculated values for pyramids of fairly simple indices for both andorite and freieslebenite, though none of these pyramids are known forms for either mineral.

Grouping the measurements of faces of the known forms together, on the assumption that the crystal measured was andorite, the results shown in the following table are obtained. The closest corresponding angle for freieslebenite is added to the last column.

TABLE 8. ANDORITE(?): COMPARISON OF MEASURED AND CALCULATED $\phi$ ANGLES OF KNOWN PRISMS

| Form | Measurements | Average of measurements | Calculated andorite | Calculated freieslebenite |
|---|---|---|---|---|
| *k*{120} | 36°32′–37°15′<br>35 29 –38 36<br>36 54 | 36°57′ | 36°27′ | {250}=34°17′ |
| *l*{230} | 44 06 –45 22<br>44 49<br>40 37 –46 11<br>45 12 | 44 32 | 44 33 | {350}=45 39 |
| *m*{110} | 54 22 –57 05<br>53 59 –58 17<br>54 17 | 55 23 | 55 54 | {560}=54 51 |
| *o*{320} | 64 03 –66 33<br>63 12 –68 12<br>61 39 –68 12<br>66 34 | 65 38 | 65 42 | {430}=66 15 |
| *n*{210} | 70 20 | 70 20 | 71 18 | |
| $\psi${510} | 82 20 | 82 20 | 82 18 | {510}=83 18 |

A closer agreement of the measured prism angles with those of freieslebenite can be obtained by turning the measured crystal 90° around the *c*-axis, though then there is no agreement between the dome faces.

TABLE 9. ANDORITE (?): COMPARISON OF MEASURED PRISM ANGLES, IF CRYSTAL IS TURNED 90° AROUND THE *c*-AXIS

| Form | 90°-$\phi$ | Freieslebenite |
|---|---|---|
| *k*{120} | 53°03′ | {450}=53°45′ |
| *l*{230} | 45 28 | {350}=45 39 |
| *m*{110} | 34 37 | {250}=34 17 |
| *o*{320} | 24 22 | [a]{140}=23 05 |
| *n*{210} | 19 40 | {150}=18 49 |
| $\psi${510} | 7 40 | — |

[a] Form not known for freieslebenite.

An idealized drawing of the crystal is shown in Figure 2. The faces of the unit prism *m*{110} are drawn as distinct faces, whereas actually they are rounded and strongly striated vertically. The forms {120}, {230}, {110}, {430}, and {320} are the common prisms, each occurring with at least three faces. The lower portions of both faces of *y*{031} are striated.

The crystal from the Ochoco district resembles in general habit Figure 2 of andorite and Figure 17 of freieslebenite, as listed in Goldschmidt's *Atlas der Krystallformen.*

The absence of any pinacoids (the measurement of face No. 5, with $\phi=87°24'$ does not necessarily demonstrate the occurrence of {100}) favors the reference to freieslebenite, for andorite crystals commonly have pinacoids present, especially the side pinacoid *b*{010}. Thus, in the 15 combinations listed by Koch (1928) *b* is present on every crystal of andorite as it likewise is in the five drawings listed in Goldschmidt's Atlas der Krystallformen. Faces of *b*{010} are frequently absent on crystals of freieslebenite.

The generally better agreement of the measured angles with those of andorite, however, would seem to favor the reference of the measured crystal to andorite. Additional and better material, though, needs to be examined before a definite identification can be made.

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# ETCH TESTS ON CALAVERITE, KRENNERITE, AND SYLVANITE

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This paper is supplementary to a comprehensive study of the gold and silver tellurides which has been carried on by Tunell and Ksanda and which is still in progress. The complex crystallography of calaverite has been thoroughly described by Goldschmidt, Palache and Peacock (1931). That of sylvanite and krennerite has long been known.

Owing to the close similarity in physical and chemical properties between calaverite, krennerite, and sylvanite, authentic specimens of any particular one of these three minerals are difficult to obtain. The resemblance between calaverite and krennerite is especially close and one cannot be certain of the identity of either of these except by measurement on the reflection goniometer or by $x$-ray study.

Authentic crystals of all three minerals were supplied by Prof. Palache and Dr. Peacock. These crystals were subsequently investigated structurally by Tunell and Ksanda by means of the Weissenberg $x$-ray goniometer (1935, 1936, 1937).

As crystallographic and $x$-ray investigations are somewhat complicated and the necessary equipment is not at the disposal of most workers, it seemed desirable to supplement these studies by a determination of etching and other tests usually made under the reflecting microscope. Accordingly, crystals of the three tellurides were mounted in bakelite in known orientations and polished in the Laboratory of Economic Geology at Harvard University under the direction of Dr. Tunell, and these specimens were lent by him to the present writer for the purpose of mineragraphic study.

The reagents commonly used in routine mineragraphic tests are 1:1 $HNO_3$, 1:1 HCl, 20 per cent KCN, 20 per cent $FeCl_3$, 40 per cent KOH, and 5 per cent $HgCl_2$. Of these reagents only nitric acid yields definite etch patterns on the above-mentioned tellurides. Previous etch tests made by Dr. Tunell indicated that concentrated nitric acid gives better results than the 1:1 reagent, hence the writer decided to conduct tests with nitric acid of both strengths.

The time of etching is an important factor in the results produced. The standard practice in routine mineragraphic tests is to etch one minute with each reagent. As this practice has long been established as regards 1:1 $HNO_3$, it was decided to choose this time for this strength of acid. On the other hand, owing to the stronger action of concentrated acid, one minute is too long, as an etch cleavage which may form with a shorter etch period, may be destroyed by etching as long as one minute.

After some experimentation, 40 seconds was the period chosen for etching with concentrated acid. The results obtained on each specimen by etching with 1:1 acid and concentrated acid respectively were totally different. This was a surprise and led to further experimentation with acid of strength midway between the two above-mentioned strengths, i.e., 3:2 $HNO_3$ (three parts by volume of conc. $HNO_3$ added to two parts of water). The time of etching with this reagent was 40 seconds. The results of these tests are shown in Figures 1 to 7.

*Calaverite.* Two specimens were investigated. One specimen shown in Figures 1*a*, 1*b*, and 1*c*, is sectioned in the orthodome zone. The other shown in Figures 2*a* and 2*b* is sectioned parallel to the side pinacoid. When these polished surfaces are etched with 1:1 acid no etch cleavage is apparent until the drop is removed by squirting a stream of water against it. When the water is removed and the surface dried, the surface of the specimen breaks up into irregular areas, each consisting of a flake a few microns thick. These tend to curl at the edges, giving the specimen somewhat the appearance of shingles on an old roof. In the orthodome section, the flakes seem to show no parallelism (Fig. 1*a*). In the side pinacoid section, the parallelism is pronounced (Fig. 2*a*). The surface of the specimen beneath these flakes is not rough, as when chalcocite is etched, but is apparently smooth. (The white areas between the flakes in Figures 1*a* and 2*a* show the unetched under-surface.)

Apparently the surface layer acts as a coating protecting the layer beneath it, in a manner somewhat analogous to the human epidermis. When this layer is removed by polishing, the former under-layer now becomes the surface layer ("epidermis") and reacts to etching in exactly the same way as the first "epidermis."

Small circular areas scattered irregularly over the surface have resisted the etching in part. These circular areas deserve further study in relation to the problems of the peculiar morphology of calaverite first described by Penfield and Ford and the adventive diffraction spots found by Tunell and Ksanda, since these resistant areas may indicate some kind of inhomogeneity. They are not visible on an unetched surface. These circular areas were too small to test separately. They do not appear when the specimen is etched with concentrated acid.

With 3:2 acid, a distinct parallel etch structure is developed (Fig. 1*b*). The areas between the etch partings tend to break off irregularly giving an appearance similar to boards on the side of an old house. The circular areas already mentioned have escaped corrosion. With concentrated acid a much more uniform etch cleavage is developed (Figs. 1*c* and 2*b*). From the excellent development of etch cleavage on the side pinacoidal section, it is probable that this cleavage is parallel to some face in the orthodome zone.

*Krennerite*. Two specimens of krennerite were available. One was sectioned parallel to the base (001). As stated by Tunell, this is analogous to the face (010) of calaverite. The results of etching this surface are shown in Figures 3*a*, 3*b*, and 3*c*. The other specimen is sectioned parallel to the plane (430) in krennerite (this plane is structurally analogous to the plane (100) of calaverite). The results of etching this specimen are shown in Figures 4*a*, 4*b*, and 4*c*. With 1:1 acid flaking is pronounced in both specimens. In the basal section two directions at right angles are distinctly discernible (Fig. 3*a*). In the other specimen the flakes are entirely irregular (Fig. 4*a*).

With 3:2 acid the two directions of etch cleavage are more pronounced in the basal section. Circular areas of apparently unetched material are scattered irregularly over the surface. Examined with a higher power, the circular areas likewise show a rectangular etch pattern, but on a much more minute scale.

When etched with concentrated acid the rectangular pattern is no longer evident on the basal section (Fig. 3*c*) but is pronounced on the other section (Fig. 4*c*). The circular areas disappear when the specimen is etched with concentrated nitric acid.

*Sylvanite*. Three specimens of sylvanite were studied. One sectioned parallel to (010) is shown in Figures 5*a*, 5*b*, and 5*c*. The second specimen, sectioned parallel to the *b*-axis, is shown in Figures 6*a*, 6*b*, and 6*c*. The third, sectioned in a random direction, is shown in Figures 7*a*, 7*b*, and 7*c*.

Sylvanite differs from calaverite in that when etched with 1:1 nitric acid the etching appears while the drop is still in contact with the surface (i.e., the acid drop does not have to be removed and the surface washed with water and dried before the etching appears).

With 1:1 acid the etching differs with the orientation. In Figure 5*a* the etching takes the form of short discontinuous cracks which give the surface a vermicular appearance. Most of these are parallel, but a small percentage show some divergence from parallelism. With 3:2 acid this effect is exactly reproduced on this specimen.

In Figure 6*a* two cleavages at right angles are shown. The vertical is more prominent than the horizontal. With 3:2 acid the two etch directions are more clearly brought out and seem to be of equal importance.

The effect of time on etching is brought out in Figures 5*b* and 5*c*. Both show etching of the same specimen with concentrated $HNO_3$; Figure 5*b* shows the result of 10 seconds etching, and Figure 5*c* shows another place on the same specimen etched 40 seconds. In Figure 5*b* only one direction is brought out. In Figure 5*c* two directions are shown. One shows prominent wide cracks relatively few in number. These probably correspond to the cleavage shown in Figure 5*b*. The other cleavage is less prominent but the cracks are closely spaced and much more numerous than the first set.

In Figure 6*c* two cleavages at right angles are shown. These seem to be about equally prominent, but the specimen seems to show some distortion, probably the result of crushing during the mounting in bakelite under pressure.

*Summary*. The results of etching the three tellurides are not as simple and conclusive as had been hoped for. The variations in results when different strengths of acid and different times of etching are employed call for control of both factors. On the other hand, the etch patterns are not capricious; each figure illustrates several experiments performed under the same conditions, and the conclusion is justified that, under the same conditions, a given specimen will yield the same etch patterns.

Calaverite and krennerite give similar patterns, but krennerite will give two etch-cleavages at right angles in certain sections whereas calaverite apparently will give an etch-cleavage in only one direction. Both krennerite and calaverite flake, and many specimens of both minerals develop circular areas that may represent spherical inclusions when etched with 1:1 $HNO_3$. Etch-cleavage in one direction indicates, but does not prove calaverite.

Sylvanite gives an etch-cleavage similar to that of krennerite but the cleavages develop while the drop is on the specimen and the surface does not flake when washed and dried.

In conclusion, etching with both 1:1 and concentrated nitric acid will usually lead to a decision whether an anisotropic gold and silver telluride is sylvanite or one of the other two minerals, calaverite and krennerite. It is difficult to distinguish calaverite from krennerite by etching with nitric acid in some cases, but if two etch-cleavages at right angles are developed the mineral is probably krennerite.

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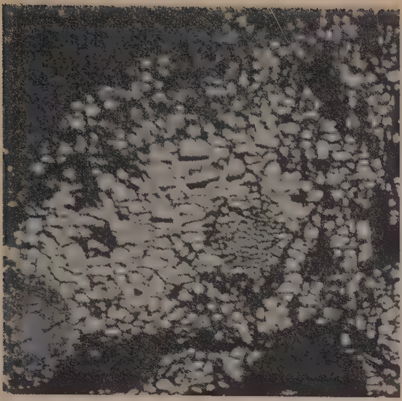
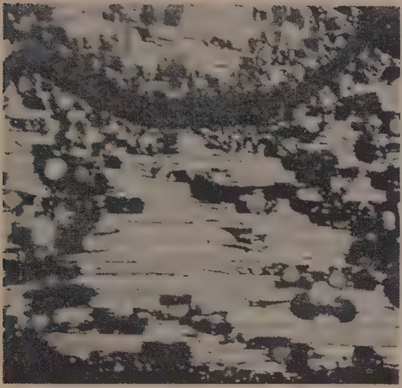


1a



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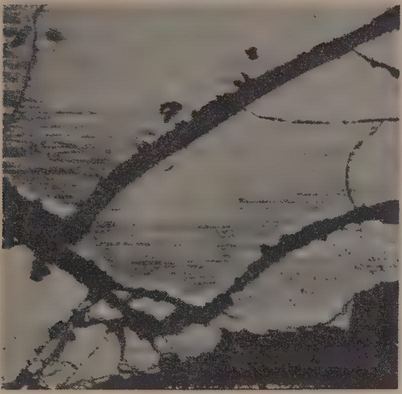

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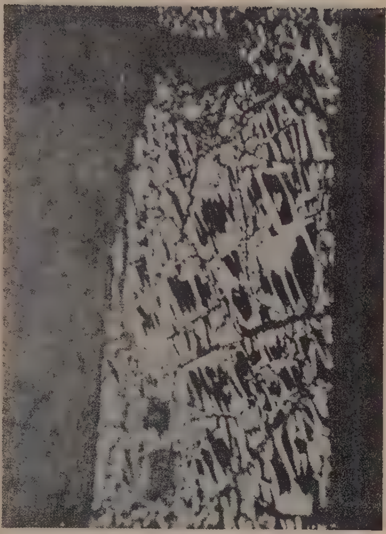

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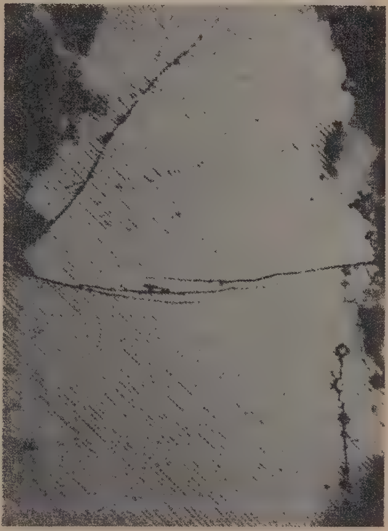


2b

PLATE I

Etch Cleavage on Calaverite

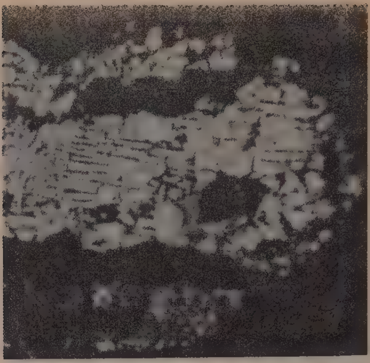
FIG. 1*a*—Calverite, Cripple Creek. Section parallel to b-axis (i.e., in orthodome zone). Section etched 60 seconds with 1:1 $HNO_3$.—×100

FIG. 1*b*—Same specimen as 1*a*. Section etched 40 seconds with 3:2 $HNO_3$.—×55

FIG. 1*c*—Same specimen as 1*a*. Section etched 40 seconds with concentrated $HNO_3$.—×55

FIG. 2*a*—Calaverite, Cripple Creek. Section parallel to 010. Section etched 60 seconds 1:1 $HNO_3$.—×52

FIG. 2*b*—Same specimen as 2*a*. Section etched 40 seconds with concentrated $HNO_3$.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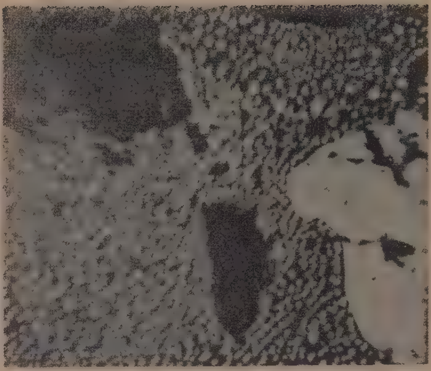
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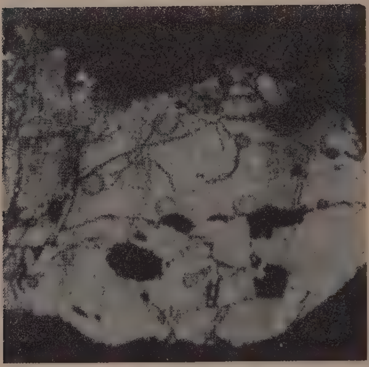
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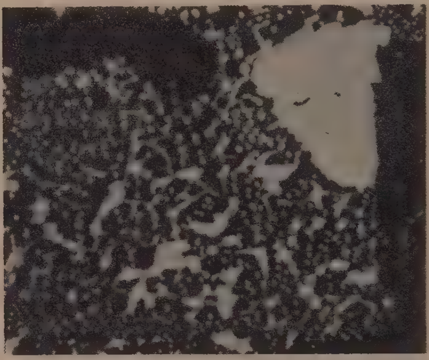
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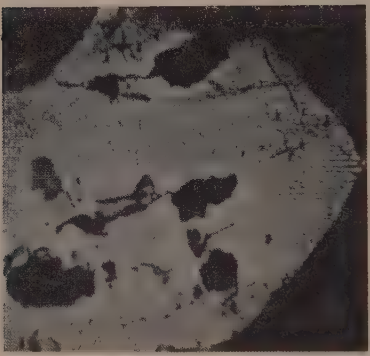
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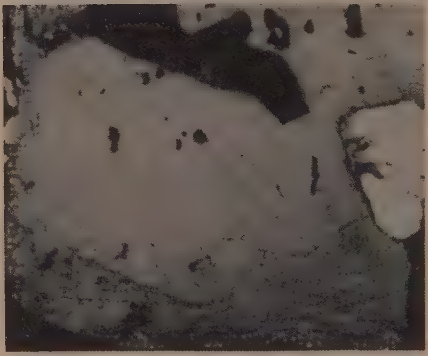

4c

PLATE II

Etch Cleavage on Krennerite

FIG. *3a*—Krennerite, Cripple Creek. Section parallel to krennerite 001 (analogous to 010 of calaverite). Etched 60 seconds with 1:1 $HNO_3$.—×87

FIG. *3b*—Same field as *3a*. Etched 40 seconds with 3:2 $HNO_3$.—73

FIG. *3c*—Same field as *3a*. Etched 40 seconds with concentrated $HNO_3$.—×95

FIG. *4a*—Krennerite, Cripple Creek. Section parallel to plane 430 in krennerite (this plane is structurally analogous to plane 100 of calaverite). Etched 60 seconds with 1:1 $HNO_3$. Small inclusion of tetrahedrite at center of right border of field is unetched. Tetrahedrite shows incipient alteration to covellite.—×87

FIG. *4b*—Same field as *4a*. Etched 40 seconds with 3:2 $HNO_3$. Surface breaks into irregular flakes showing no parallelism.—×73

FIG. *4c*—Same field as *4a*. Etched 40 seconds with concentrated $HNO_3$.—×55

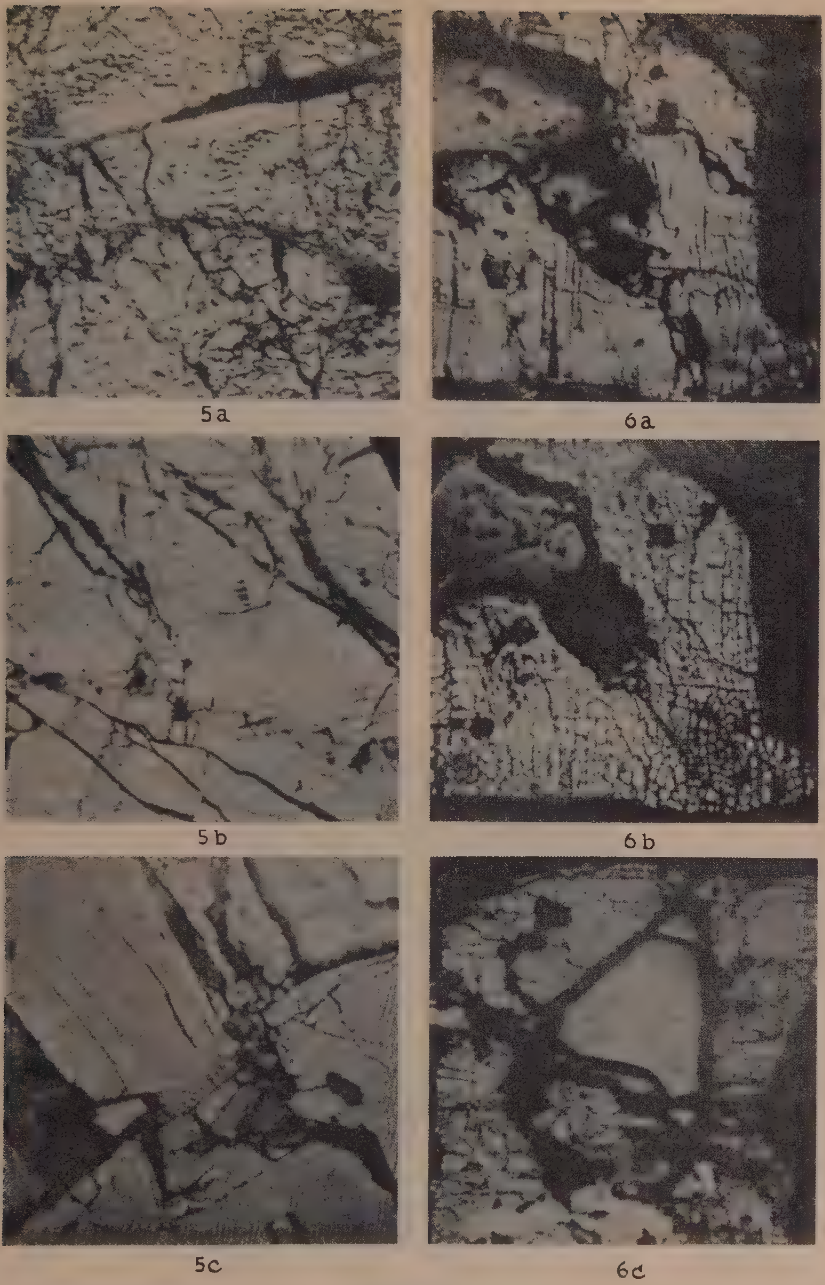

5a 6a 5b 6b 5c 6c

PLATE III

Etch cleavage on Sylvanite

FIG. 5*a*—Sylvanite, Cripple Creek. Section parallel to 010. Etched 60 seconds with 1:1 $HNO_3$.—×87

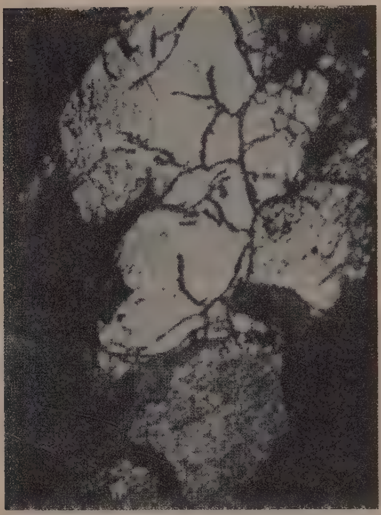
FIG. 5*b*—Same specimen as 5*a*. Etched 10 seconds with concentrated $HNO_3$.—×87

FIG. 5*c*—Same specimen as 5*a*. Etched 40 seconds with concentrated $HNO_3$.—×210

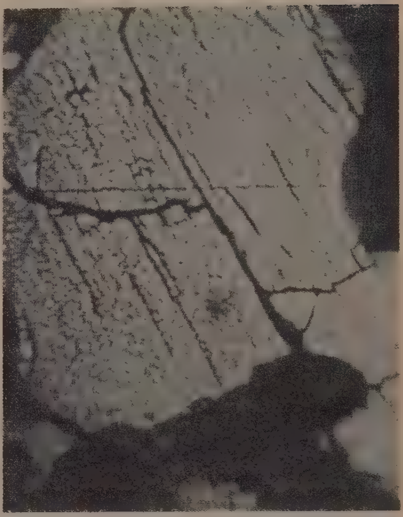
FIG. 6*a*—Sylvanite, Cripple Creek. Section parallel to *b*-axis. Etched 60 seconds with 1:1 $HNO_3$.—×87

FIG. 6*b*—Same field as 6*a*. Etched 40 seconds with 3:2 $HNO_3$.—×87

FIG. 6*c*—Same specimen as 6*a*. Etched 40 seconds with concentrated $HNO_3$.—×55



7a



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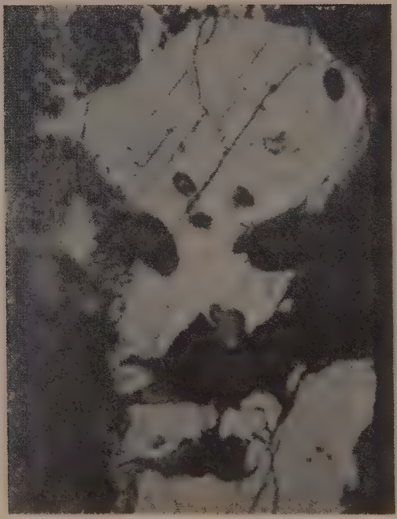

7c

PLATE IV

Etch Cleavage on Sylvanite

Fig. 7*a*—Sylvanite, Săcărâmbu (Nagy-Ág), Transilvania. Random section. Etched 60 seconds with 1:1 $HNO_3$.—×87

Fig. 7*b*—Same specimen as 7*a*. Etched 40 seconds with 3:2 $HNO_3$.—×210

Fig. 7*c*—Same specimen as 7*a*. Etched 40 seconds with concentrated $HNO_3$.—×95

# SIMPLIFIED GRAPHIC METHOD OF DETERMINING APPROXIMATE AXIAL ANGLE FROM REFRACTIVE INDICES OF BIAXIAL MINERALS

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## INTRODUCTION

The mathematical interrelation between axial angle, optic sign, and refractive indices of biaxial minerals gives a method of determining axial angle and sign, and provides a check on the consistency of index determinations by the immersion method. This relation is expressed exactly by the accurate equation and approximately by Mallard's simplified form of that equation, both of these being given in standard textbooks on the subject (Johannsen, 1914, pp. 103–104; Rosenbusch and Wülfing, 1924, pp. 119–121; Winchell, 1931, pp. 159–160). In determinative mineralogy, the approximate equation is more convenient to use, and generally is sufficiently accurate for practical purposes. Its application is facilitated by the graphic solution introduced by Wright (1913, pl. 6; 1911, pl. 9).

Wright's graphic solution, helpful though it is, retains certain of the disadvantages, or inconveniences, of the equation on which it is based. It requires that partial birefringences be computed first, and that optic sign be noted indirectly, by inspection. It gives $V$ rather than $2V$, and, unless the terms are reversed, it always gives $V$ with respect to the same fixed axis of the indicatrix, regardless of optic sign. To the beginner this is a source of considerable confusion, and it is a real inconvenience even to the experienced worker, leading frequently to a neglect of the method when it might well be used as a check on laboratory determinations.

In the graphic method here presented these disadvantages are eliminated. Partial birefringences need not be computed nor their ratios noted. A sliding scale carrying a range of values for refractive indices is simply aligned with a chart, and reference lines are traced through the chart to an upper scale on which the optic sign and axial angle are read directly.

## THE SIMPLIFIED GRAPHIC METHOD

The graphic method here described employs two separate parts, a graphic plot, or chart, and a sliding scale which is adjusted to the chart for each determination.

*The Chart.* The chart (figure 1) is an adaptation of Wright's graphic solution (1913, pl. 6) for the equation:

$$\tan^2 V_\alpha = \frac{\gamma - \beta}{\beta - \alpha}.$$

Wright's original plot forms the central square, or grid, of the present chart. Lines representing values along the abscissa and ordinate of this square are projected to a straight line, or base line, which makes angles of 45° with the sides of the square. The radial lines of Wright's plot, and an additional complementary set of similar lines, are projected to an upper straight line, or scale, parallel to the base line. On this upper scale the values of $2V$ for positive minerals are read on the right side of the central point, and for negative minerals on the left side. Angles used in plotting the radial lines were calculated from the equation:

$$A = \arctan \tan^2 V$$

where $A$ is the angle between the nearest side of the grid and the radial line leading to a particular value for $2V$. For convenience of any who may wish to redraft the chart, the calculated angles are listed in Table 1.

*The Sliding Scale.* The sliding scale is simply a linear scale on which the values for refractive indices within a given range are plotted in proportionate units. The unit value, 0.001, may range from one millimeter to one centimeter. Numerical values are plotted from left to right in ascending order.

In using the graphic method, maximum ease and accuracy of reading are attained when, in the reading position, one (or both) of the indices on the sliding scale falls well toward an end of the base line on the chart. Consequently, for minerals of low birefringence, it is desirable to employ a sliding scale based on a larger unit value than for minerals of high birefringence. For the latter a single scale, such as the upper one in figure 1, may suffice to cover the ordinary range. For the former, it is convenient to have a series of overlapping scales based on a larger unit value, or values. The lower scale in figure 1 is a representative example. If prepared scales are not practicable, a simple substitute is easily made by marking off on a strip of cross section paper the values for any particular set of indices, in equal units of any convenient magnitude.

## PROCEDURE

Procedure in using the graphic method is suggested by the skeletonized guide sketch accompanying the chart, and is summarized below.

1. A sliding scale is selected which has a range adapted to the indices of the mineral considered. Lacking a suitable scale already drafted, the

values of the indices may be marked off in proportionate units on a strip of cross section paper.

2. The sliding scale is moved along the base line of the chart until the value of $\beta$ coincides with the medial line of the chart.

3. Converging lines leading from the values of $\alpha$ and $\gamma$ on the sliding scale are traced to their mutual intersection in the central grid. This step is facilitated by the use of a transparent celluloid square, or even of a cardboard square.

4. The radial line passing through the above-determined intersection is traced to the upper scale, on which optic sign and axial angle are read directly.

TABLE 1. ANGLES ($A$) PLOTTED ON THE CHART FOR VARIOUS VALUES OF $2V$

| $2V$ | $A$ | $2V$ | $A$ |
|---|---|---|---|
| 0 | 0° 0′ | 54 | 14°33′ |
| 10 | 0 26 | 56 | 15 47 |
| 20 | 1 47 | 58 | 17 05 |
| 22 | 2 10 | 60 | 18 26 |
| 24 | 2 35 | 62 | 19 51 |
| 26 | 3 03 | 64 | 21 20 |
| 28 | 3 33 | 66 | 22 52 |
| 30 | 4 06 | 68 | 24 28 |
| 32 | 4 42 | 70 | 26 07 |
| 34 | 5 20 | 72 | 27 50 |
| 36 | 6 02 | 74 | 29 35 |
| 38 | 6 46 | 76 | 31 24 |
| 40 | 7 33 | 78 | 33 15 |
| 42 | 8 23 | 80 | 35 09 |
| 44 | 9 16 | 82 | 37 05 |
| 46 | 10 13 | 84 | 39 02 |
| 48 | 11 13 | 86 | 41 01 |
| 50 | 12 16 | 88 | 43 00 |
| 52 | 13 23 | 90 | 45 00 |

## ACCURACY

The accuracy of this method is dependent on three factors: (1) the accuracy of the approximate equation, (2) the precision attained in laboratory determination of indices, and (3) the accuracy of the chart itself. The effects of each of these is considered below.

*Accuracy of the approximate equation.* Certain errors inherent in the approximate equation were noted by Wright (1913, pp. 530–532), and have been analyzed in detail by Larsen and Berman (1934, pp. 6, 7). Summarizing briefly, the magnitude of these errors varies directly with birefringence and axial angle, and inversely with refringence. For a mineral whose lowest index is 1.50, the maximum error is less than 1° when total birefringence is 0.05, less than 1°30′ when total birefringence is 0.10, and nearly 4° when birefringence is 0.30. As $\alpha$ increases, the maximum error for any given value of total birefringence decreases slightly. For constant values of refringence and birefringence, the error is maximum when $2V$ is 90°, and becomes negligible as $2V$ approaches zero. Correction factors for compensating these errors are given by Larsen.

*Errors in Laboratory Determinations.* Obviously, results from the graphic method can be only as accurate as the data used. Index determinations by the immersion method have an accuracy which varies roughly from ±.003 to ±.001, or less, depending on the skill of the worker, the equipment used, and the nature of the material studied. Errors arise from (1) dispersion, (2) incorrect orientation of the mineral for particular readings, (3) failure to match liquid and mineral exactly, and (4) inexact calibration of the liquid. The errors arising from dispersion may be eliminated by using monochromatic light. Correct crystallographic orientation of mineral grains may be assured by obtaining centered interference figures, by using universal stage methods, or, in certain instances, by noting cleavages and extinction angles. Close matching of liquid and mineral may be attained by chance, by decreasing the interval between successive liquids in the series, by mixing liquids, or, better, by using index variation methods. Proper calibration of the liquid depends mainly on care in comparing temperatures at the time of calibration and at the time of mineral determination, and on guarding against deterioration of the liquid during the interval between these two steps. A consideration of these several factors provides a basis for evaluating the accuracy of data in particular instances, Only when the total birefringence of the mineral is much greater than the maximum possible error in index determinations can a very close approximation to the true axial angle be expected from any mathematical method.

*Accuracy of the Chart Itself.* The accuracy of the chart is determined both by the precision with which it is constructed and by the degree of exactness with which it may be read. The former factor is relatively constant throughout the chart, the lines being drafted with an accuracy of about ±5 minutes of arc. Errors in $2V$ introduced by possible deviations of this amount increase toward the lower ends of the scale, but, in practice, are negligible.

The ease and exactness with which the chart may be read varies with the spacing of the radial lines, and thus is different for different parts of the chart. Greatest exactness is possible where the radial lines are well separated, and least exactness where they are crowded. Crowding occurs in two gradational zones—toward the two sides of the central grid, affecting only those radial lines representing the lower values of $2V$, and toward the central or converging point of the radial lines, affecting all lines. The consequences of the former are inherent in the formula on which the chart is based, and unavoidable, but concern only a relatively small group of minerals. The effects of crowding at the central zone, however, may be avoided by selecting, for each determination, a sliding scale which throws the intersection point beyond the crowded area. Used thus with discrimination, the chart, throughout the greater part of its range, will give a value of $2V$ matching to the nearest degree that given by calculation with the approximate equation.

Considering all sources of error, it may be stated that the graphic method is most satisfactory in determining axial angle for minerals whose total birefringence is neither very low nor unusually high—ranging, roughly, from a few units in the second decimal place to a few units in the first decimal place, the lower limit varying with the degree of precision attained in index determinations. Correct optic sign is given for all minerals whose axial angle does not fall very near to 90°.

## Applications

The graphic method is useful both as a means of determining axial angle and optic sign, and as a check on the general consistency of optical data when all constant are determined directly. For minerals on which interference figures are impossible to obtain, it constitutes the only method of determining $2V$ and sign (excepting, of course, the equivalent calculations or the use of universal stage methods). Similarly, if two indices, axial angle, and optic sign are known, the graphic solution may be used to determine the third index. As suggested by Larsen and Berman (1934, p. 6), however, a more general application lies in using the method as a check on the mutual consistency of optical constants when all are determined directly by standard methods. If any one (or two) of the set falls beyond the position on the chart prescribed for it by the others, an error is indicated, and a consideration of the relative degree of certainty with which the several constants were measured may suggest the source of the error. Both of these applications of graphic methods in connection with the universal stage and the double variation method have been noted by Emmons in Winchell (1931A, pp. 235, 239; 1931B, pp. 132, 140, 142).

To the teacher, the graphic chart provides a means of repeatedly

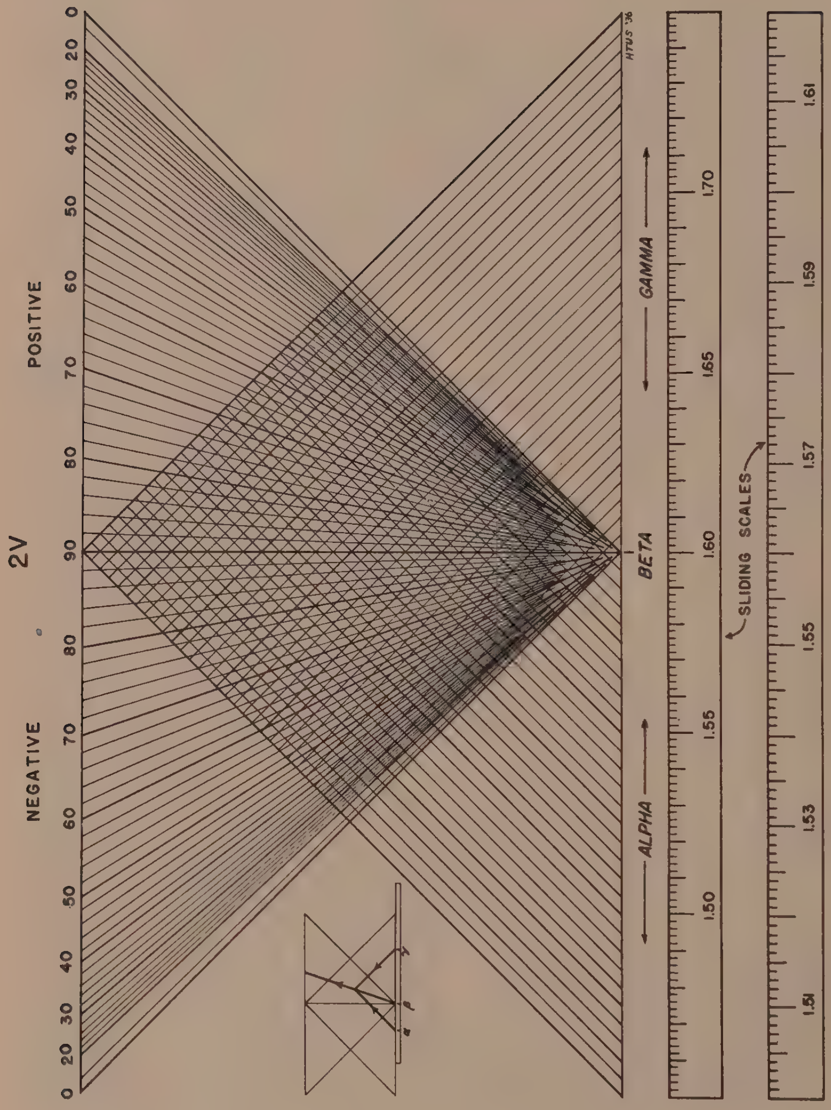
2V
POSITIVE
NEGATIVE
0
20
30
40
50
60
70
80
90
80
70
60
50
40
30
20
0
HTUS '36
GAMMA
BETA
ALPHA
1.70
1.65
1.60
1.55
1.50
1.61
1.59
1.57
1.55
1.53
1.51
SLIDING SCALES
α
β
γ

Fig. 1

emphasizing the fundamental interrelation of important optical constants, and thus of encouraging in the student a genetic rather than an empiric approach to laboratory procedure.

## ACKNOWLEDGMENTS

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# SOME MINERAL NAMES

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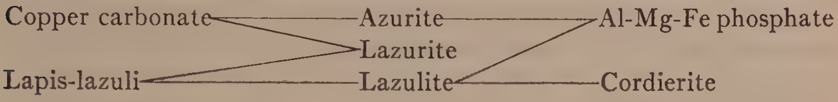
When I make the bold assertion that *alcohol* is a mineral name, it may perhaps be thought that I have partaken too freely of liquid refreshment, so disturbing to a balanced judgment. Nevertheless, this is a very early name for the mineral now known as stibnite or antimonite.

In Arabic *al-kohl*, meaning "the colouring" (*al* being the definite article), is the black powder used for darkening the eyelids. In the theatrical profession the pigment used for this purpose is still called kohl. Francis Bacon in his "Sylva sylvarum; or a naturall historie" (1626, p. 739) says: "The Turkes have a Black Powder, made of a Mineral, called Alcohole; which with a fine long Pencil they lay under the Eyelids." In the course of time the name alcohol became extended to include any fine impalpable powder, especially such as can be obtained by sublimation; and as late as 1812 Sir Humphry Davy mentions "alcohol of sulphur" for what is now commonly known as "flowers of sulphur." As the operation of distillation is very similar to that of sublimation, the name came to be extended to essences and spirits; and in the sixteenth century "spirit of wine" was called "alcohol of wine" by alchemists. This "elixir of life" was later called simply alcohol; and now the name is extended to liquors containing only a small percentage of $C_2H_5OH$.

This is a very striking example of the gradual change which, in the course of time, words may undergo in their meaning. About a hundred years ago a further extension in the meaning of alcohol was introduced by chemists for a whole series of organic compounds containing the group (OH). This hydroxyl group is now fashionable in mineralogy, so perhaps the name alcohol may again come back to minerals.

Other early names for the mineral stibnite were *stimmi* or *stibi* (Greek) and *stibium* (Latin), which were applied to a cosmetic used for darkening the eyelids and eyebrows. On this account the material was also known in Greek as *platyophthalmon* ("wide eye")—as recorded by Dana. Whether or not these are earlier names than the Arabic *al-kohl* I have not been able to discover; nor is this of much consequence in the present connection, for it would be useless, indeed foolish, to insist here on the law or priority. The name stibnite, due to J. D. Dana (1854), is a modification of stibine as originally given by F. S. Beudant (1832) from the Latin. Stibnite is good; but stibine is still used in French, and estibina in Spanish. The name antimonite, given by W. Haidinger in 1845, was already in use in 1834 as a chemical name for salts of antimonious acid.

Blue minerals have suffered a series of misfortunes in their names. Azurite, lazurite, and lazulite have each been indiscriminately applied to two minerals; and each of these minerals has received two of these names. The puzzle is to remember which is which.



These names are all derived from the Persian word *lazhward*, meaning blue colour and also applied to lapis-lazuli. Some unscholarly scribe in the middle Ages, confusing the Persian with Arabic, dropped the initial letter, evidently thinking that this was the definite article. So now we have the words azure and lazure, both of the same derivation and meaning something blue. Mineralogists have added further to the confusion., The blue copper carbonate mineral, early known as cuprum lazureum. cæruleum montanum, azure copper ore, etc., was named azurite by F. S Beudant (1824), lasur by W. Haidinger (1845), and lazurite by F. Kobell (1853). But the name azurite had earlier been used by R. Jameson in 1805 for the blue phosphate of aluminium, magnesium, and iron, now known as lazulite (M. H. Klaproth, 1795). Lazule (John Bullokar, 1616) and lazulite (Macaulay, 1849, "enshrined in lazulite and gold") are old names for lapis-lazuli; and the essential blue constituent of this stone has been named lasurite (W. C. Brögger and H. Bäckström, 1890) and lazurite (E. S. Dana, 1892). The name lazulith (E. F. Scholtheim, 1801) has also been applied to cordierite (=iolite=dichroite).

Confusion such as this indicates that it will be well to start afresh. But rather than inventing a new set of names, I select the following old names as suitable. Chessylite (H. J. Brooke and W. H. Miller, 1852) has been applied to no other mineral but the blue copper carbonate; mollite (G. A. Bertele, 1804), after Baron C. E. von Moll (1760–1838), to none other than the Al-Mg-Fe phosphate; while lazulite, rather than lasurite or lazurite, is obviously the best name for the lapis-lazuli mineral. Azurite is a good name; but to recognise priority and use it in its original sense would only cause further confusion. At the present time, as I write, "az-u-rite" is a trade-name for a blue-black ink.

Lapis-lazuli was called sappheiros and sapphirus by the Greeks and Romans, and the latter form was used in this sense by G. Agricola as late as 1546. This name has since been transferred to the blue variety of corundum, the now well-known sapphire, which to the Greeks and Romans was known as hyakinthos and hyacinthus. Many other old names for gemstone minerals have had a chequered career. Chrysolite (Greek *chrysos*, gold, and *lithos*, stone) has done duty for topaz, beryl, yellow olivine, quartz, corundum, etc. Its association with green olivine is suspicious; and as a name for a mineral species it may now well be allowed to become obsolete. Printers' readers are always troubled with chrysolite and chrysotile (=serpentine-asbestos).

Another familiar confusion, with duplication of names, is with the zinc carbonate and silicate minerals. This can be most simply straightened out by adopting the name smithsonite for the carbonate and hemimorphite for the silicate.

Smithson, 1803—Calamine——Brongniart, 1807
$ZnCO_3$—Beudant, 1832—Smithsonite——Miller, 1852——$H_2Zn_2SiO_5$
Hemimorphite—Kenngott, 1853

The name siderite (from the Greek *sidēros*, iron) has been used in many different senses and applies to several different minerals. In Latin, *siderites* was loadstone (=magnetite) and also a precious stone; the adamas siderites of Pliny being probably sapphire. The great Oxford Dictionary gives an English quotation under date 1579 for syderite as applied to loadstone. Other meanings are for iron ore, ironwort (a plant), and meteoric iron. The name has also been applied to the following minerals:

Siderite of T. Bergman (1790) =pharmacosiderite
Siderite of C. E. Moll (1797) =blue quartz
Siderite of C. E. Moll (1799) =lazulite=mollite
Siderite of J. Pinkerton (1811) =hornblende
Siderose of S. F. Beudant (1832)=chalybite
Siderite of W. Haidinger (1845)=chalybite

The choice of a name for iron carbonate here lies between chalybite (E. F. Glocker, 1847) and siderose, neither of which has been applied to any other mineral.

There is a strange similarity between the Greek *sidēros* (iron) and the Latin *sidus*, *sideris* (star), which is reflected in the English words sidereal, siderous (star-like and ferreous), and siderite. A connection between the names for falling stars (thunderbolts or meteorites) and iron has been traced in some ancient languages; and here the words may have had a common origin in some language previous to Greek and Latin, when meteoritic iron was the only iron available to early man. If this is so, then meteoritic iron has a strong case for priority in the use of the name siderite.

Felspar or feldspar? This is a minor problem still undecided amongst English mineralogists. Neither form is strictly correct. The name as originally given by D. Tilas in 1740 was feldtspat. He gave no derivation, but no doubt the name has reference to the presence of the spar (spath) in tilled fields (Swedish, feldt or fält) overlying granite. Other Swedish forms are feltspat (J. G. Wallerius, 1747) and fältspat (A. F. Cronstedt, 1758). The German translation (1750) of Wallerius has feldspath, and the English translation (1772) of Cronstedt was field-spar. The field idea comes also into some other languages: földpátak (Hungarian) and polevoi shpat (Russian). R. Kirwan in the first edition of his "Elements of Mineralogy" (London, 1784) has felt-spar; but in his second edition (1794) he gave the name as felspar, evidently realising that this important rock-forming mineral has more to do with rocks than with fields. If any change from felspar is really needed, this should be to the original Swedish form feldtspar or feltspar, without stopping half-way at the German form feldspar. An interesting historical paper on this name has been given by N. Zenz n (Geol. För. Förh. Stockholm, 1926, vol. 47 for 1925, p. 390).

Another mineral with different spellings in current use is chalcosine or chalcocite. The original form chalcosine of F. S. Beudant (1832), from the Greek *chalkos*, copper, is followed in European languages (French, English, Italian); chalcosina (Spanish) and Chalkosin (German). The alteration to chalcocite was made without sufficient reason by J. D. Dana in 1868. In this etymological atrocity the letter *c* is given three different values: the first *c* is part of *ch*, which in Greek (also Russian, Czech, and Spanish) is a separate letter of the alphabet; the second is the Greek *k*; and the third is pronounced as *s*.

In tracing the history and derivations of mineral names A. H. Chester's "Dictionary of the names of minerals" (New York 1896) is of the greatest help. This work was done by him in connection with the "New English Dictionary" (Oxford, 13 vols., 1884–1933) in which he was responsible for most of the mineral entries. This monumental work gives actual quotations through the centuries from the year 1000.

# A CONTRIBUTION TO THE STUDY OF ACCESSORY MINERALS OF IGNEOUS ROCKS

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## Introduction

Within the last few years ever increasing interest has been shown in the possibility of using the accessory minerals of igneous rocks for purposes of correlation. It is perhaps unfortunate, however, that before attempts were made to use the accessories for this purpose, the methods were not subjected to a thorough test on some group of igneous rocks whose age was beyond doubt. For some years the writer has been endeavouring to apply such a test. The method used has been to examine the heavy mineral suites of a number of granites, including, in particular some single composite granite mass of known age: in the case of the latter to see what amount of variation there is between the suites of specimens collected from different positions and heights in the same intrusion: and then to compare the results with those obtained from other granites with a view to determining:

(a) Whether the range of variation in the heavy minerals of one composite granite mass is less than that between two granites of different ages.

(b) The amount of variation in granites of the same age, whose size and cooling history are different.

The present contribution deals briefly with the first part of the subject, the study of the accessories of a single composite intrusion.

## Methods Employed

Unfortunately methods of separating and investigating the accessory minerals of igneous rocks are far from standardised, and the comparison of independent results is consequently quite unnecessarily complicated. The author has, in the main, modelled his methods on those of A. W. Groves (1927A, B; 1930), only departing from them where it seemed that some alteration was desirable.

In collecting from any igneous mass specimens were chosen to cover as wide a range of texture and composition as possible. Approximately 100 grams of each rock were crushed with frequent sieving through a $\frac{1}{2}$ mm. mesh sieve, and the powdered rock washed to remove rock flour.

Twenty grams of each sample were separated quantitatively in a funnel filled with bromoform (Sp. Gr. 2.88). The proportion of "heavy minerals" obtained in this way and expressed as a percentage is the "Index Figure" to which Groves attaches considerable importance. The heavy crop (in the case of acid igneous rocks) frequently consists of a gram or more of material which is much more than can be conveniently mounted. Accordingly it was separated by means of the electro-magnet into two fractions referred to below as magnetic and non-magnetic fractions. The whole of the non-magnetic residue was in every case mounted and examined; and it was with the object of obtaining an amount which could conveniently be mounted in its entirety that the weight of 20 grams was selected as the standard quantity for separation. The danger that so small an amount would not furnish a representative sample of the rock was as far as possible obviated by always crushing 100 grams and well mixing the powder before weighing out the 20 grams.

The magnetic fraction of the heavy crop was treated with a small horse-shoe magnet, and the material extracted tested for pyrrhotite: sufficient of the remainder to fill half a dozen slides was mounted for examination. In most cases, owing to the deep colour of the magnetic accessories, it was found desirable to crush them further to pass a $\frac{1}{4}$ mm. sieve before mounting.

In work of this kind, by far the most difficult task that faces the investigator is that of indicating the amounts of the several minerals present. Many workers have made no attempt to do this and have been content to include such terms as "plentiful," "scarce," or "local" in the description of the minerals. Others, including Groves, estimate proportions by eye, dividing the minerals into a number of categories of abundance: Groves has five of these, namely—Abundant, Very Common, Less Common, Scarce, Rare. The method has obvious limitations, introducing as it does the personal factor to a great extent. A distinct advance is made by J. T. Stark (1934) in a study of certain granites from Central Colorado. After separating in bromoform he weighs the sample, extracts the magnetite by means of a horse-shoe magnet and weighs the residue. The latter is mounted and every grain counted. The result is an accurate quantitative record of the heavy minerals present: but the method is only applicable to rocks poor in ferro-magnesian minerals.

The author's earliest efforts at estimating mineral proportions were similar to those of Stark. After separation by means of the electro-magnet, the two fractions were weighed and counts made of the whole of the non-magnetic material and of half a dozen slides mounted from the magnetic residue. The results when recorded give a series of mineral analyses averaging 90 per cent ferro-magnesian minerals, 5 per cent iron ores, and the remaining 5 per cent divided among some dozen or more accessory minerals. As will be seen by referring to the specimen analysis of the Jersey "Newer Granite" from La Moye, under this system the very minerals which it is desired to study are completely overshadowed by the less significant ferro-magnesians and iron ores.

In consequence of the obvious disadvantages of this method it was decided to count the minerals of the non-magnetic fraction only. Of the minerals in the magnetic fraction, the ferro-magnesians in most cases are not accessories, and are better studied in thin sections than in "crushes." The latter remark also applied in a minor degree to magnetite, pyrrhotite and ilmenite, the other common constituents of the magnetic fraction: but in addition it is an extremely difficult matter to identify small grains of these minerals and the result of counts would not be sufficiently accurate to justify the extra time and labour involved.

The procedure finally adopted by the author is therefore as follows:

(1) To examine both magnetic and non-magnetic fractions and to record all mineral species present in the heavy crop.
(2) In the description of minerals, to concentrate on the true accessories, paying minor attention to such species as biotite and hornblende, which flood the sample.
(3) By counting, to calculate accurately the proportions of the minerals in the non-magnetic fraction.

In evolving this method, the author has had the following three aims in view:

(a) The procedure adopted must be applicable equally readily to both acid and basic rocks;
(b) Some more accurate quantitative data than that provided by Groves must be obtained;
(c) The more laborious and involved the method, the less the chance of other workers conforming to it. Consequently, repeated separations by the electro-magnet and various heavy liquids have been avoided.

As an example of the advantage of the "counting method" over the method of eye-estimation, an analysis of the heavy minerals of the La Moye granite from Jersey in the Channel Islands (average of half a dozen specimens) is compared with one given by Groves (1927 B) (average of two samples). In the following table are set out:

(a) Minerals divided into five categories by eye-estimation (as determined by Groves).
(b) Mineral percentages as determined by the author by grain counts.
(c) Minerals divided into five categories on basis of percentages in column (*b*).

| | (*a*) | (*b*) | (*c*) |
|---|---|---|---|
| Biotite | 5 | 59.46 | 5* |
| Hornblende | 5 | 24.78 | 5* |
| Chlorite | 3 | 4.81 | 4 |
| Magnetite | 4 | 2.82 | 4* |
| Ilmenite | 3 | 0.96 | 3* |
| Limonite | — | 1.24 | 3 |
| Pyrite | — | 0.14 | 1 |
| Zircon | 4 | 0.60 | 2 |
| Apatite | 4 | 0.69 | 2 |

| | | | |
|---|---|---|---|
| Sphene | 4 | 0.91 | 3 |
| Fluorite | 5 | 0.91 | 3 |
| Topaz | 1 | 0.40 | 2 |
| Tourmaline | — | 0.02 | 1 |
| Muscovite | — | 0.03 | 1 |
| Rutile | — | 0.06 | 1 |
| Sillimanite | 1 | 0.02 | 1* |
| Epidote | 3 | 0.71 | 2 |
| Clino-zoisite | 3 | 0.19 | 1 |
| Opaque grains (unidentified) | — | 1.60 | |

* Indicates mineral which falls into same category in both columns (*a*) and (*c*).
Groves' five categories represent:
5. Abundant. 4. Very Common. 3. Less Common. 2. Scarce. 1. Rare.

The discrepancies between columns (*a*) and (*b*) are obvious. For example Category 5 includes biotite, hornblende and fluorite, with percentages of 59.46, 24.78 and 0.91 respectively: while Category 3 includes chlorite, ilmenite, epidote and clino-zoisite (4.81, 0.96, 0.71 and 0.19 per cent). In column (*c*) the author has attempted to apply Groves' indices of relative abundance to the percentages and in respect of only five out of the eighteen mineral species listed do the two columns (*a*) and (*c*) agree. It is surely evident that not only is eye-estimation not sufficiently delicate for the work in hand, but that the method is positively inaccurate and misleading.

In addition to the counting of the mineral species in the nonmagnetic fraction, the author has felt that some quantitative methods should be applied to the widespread zircon and apatite which often possess distinctive and easily recognisable varietal features. The difficulty was to decide which features should be selected for quantitative study: since there are generally some half a dozen of more—colour, size, crystal form, presence or absence of inclusions, zoning, etc.—all of which vary independently of one another. In any sample there will be certain varietal peculiarities which appear to merit quantitative study—e.g. the ratio of dusky zoned zircons to clear zircons, or the ratio of apatites with rod-like cores to those without. But often a ratio so easily calculable in one rock is quite obscure in another—e.g., the zircons may form a regular series from the clear to the dusky variety: yet for purposes of comparison it is essential that the same ratios be calculated for every rock type. The author has selected the following, since they can readily be calculated in any sample:

(1) Percentage of five types of zircon present:—
    (a) Roughly equidimensional crystals.
    (b) Short stout crystals—ratio of length to breadth between 1:1 and 2:1.
    (c) Medium elongated crystals—ratio of length to breadth between 2:1 and 4:1.

   (d) Very elongated crystals—ratio of length to breadth greater than 4:1.
   (e) Anhedral grains.

(2) Percentages of the following types of apatite:—
   (a) Stout prismatic crystals—ratio of length to breadth less than 4:1.
   (b) "Needle shaped" crystals—ratio of length to breadth greater than 4:1.
   (c) Anhedral grains.

(3) Relative proportions of euhedral and anhedral apatite.

(4) Relative proportions of apatite and zircon.

## THE GRANITES OF THE MOURNE MOUNTAINS

After consideration of various possibilities it was decided that among British granites, the most suitable example of a large composite intrusion was the Tertiary complex of the Mourne Mountains in County Down, Northern Ireland. The area has been described in detail by J. E. Richey (1927), who recognises four types of granite marking successive (and closely connected) intrusions resulting from ring fracturing followed by subsidence of a central block: for the full details the reader is referred to Richey's paper.

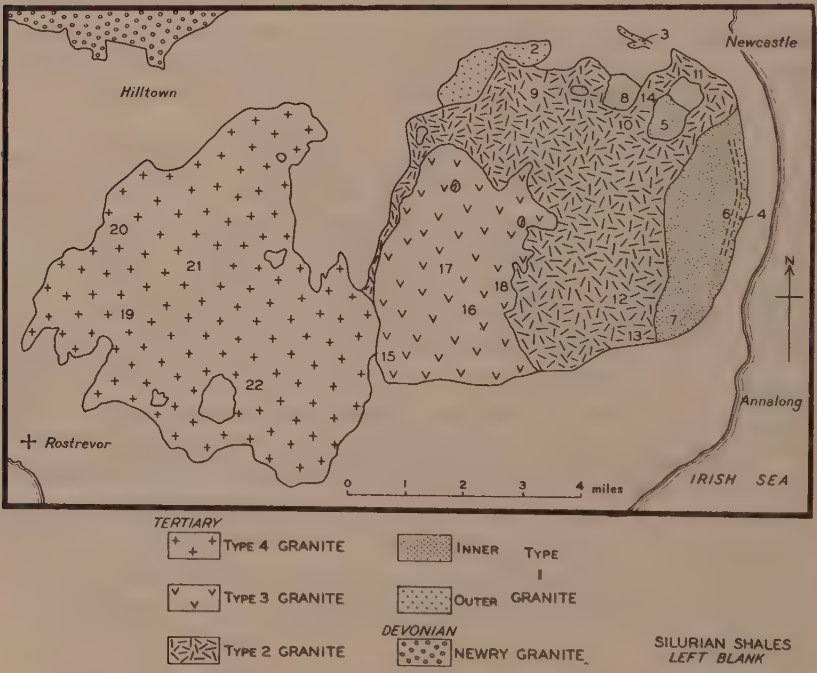

FIG. 1. Map of Mourne Mountains granite complex, to show location of samples.

*The Heavy Minerals.* On Richey's map (Fig. 1) are marked the 22 localities from which specimens of the granite were collected. In Table 1 the heavy minerals present in each sample are recorded: the percentages of the non-magnetic heavy accessories are given in Table 2: while Table 3 contains the quantitative data recording the types of zircon and apatite present.

For purposes of comparison the most prominent characteristics of the suites of the four types of granite are listed together in Table 4. It will be seen that there are no clear cut differences between the four suites. There is not a single case of any mineral, or even a variety of a mineral which is present in all the samples of any type and absent from all the samples of another. In the case of the zircons there is no variety which is dominant in all the samples of any one granite type. The most one can say is that in the majority of samples such a variety of zircon is dominant. With minerals like sphene, epidote and the pneumatolytic group, the distinctions are even more ill defined. Consequently the author feels convinced that in the majority of cases it would be impossible to refer a specimen from the Mourne Mountains to any of the four types by a study of its accessory minerals alone. And this despite the fact that it is generally possible to distinguish the several types in hand specimen and thin section. Admittedly in certain very favourable circumstances the accessory minerals might yield some evidence as to the type of granite being examined. For example, abundant hornblende, decided dominance of the medium elongated type of zircon and absence of epidote would strongly suggest a Type 1 granite. On the other hand absence of these characteristics (as for example in Sample 6) is no evidence that the granite belongs to one of the other types.

Examination of Table 4 suggests that Type 3 has features sufficiently distinctive to impress the stamp of individuality upon it. A low percentage of zircon (say $<15$ per cent) together with complete absence of apatite and an Index Figure not above 2.1 (the maximum value obtained for a Type 3 granite) should surely be sufficient to determine a sample as belonging to this group. But these three criteria are all exhibited by Samples 3 and 4 (Type 1 granite) and Sample 10 (Type 2 granite). In at least two of these cases examination of a single thin section would have been sufficient to place them in their correct group. It thus appears that, as far as the distinguishing of the four intrusions of the Mourne Mountains is concerned, the complicated process of isolating, examining and counting the accessory minerals is far less accurate than the simple and old established method of relying on thin sections. The evidence all goes to show that not only can rocks alike in hand specimen and thin section yield distinctive heavy minerals suites, but also that rocks markedly different in hand specimen and thin section can yield very similar heavy mineral suites. In other words, similarities and differences in the essential mineral content of these rocks are *not* reflected in their accessory minerals.

*Variation in Fluorite and Zircon within the Complex.* Careful record has been kept of the approximate altitude from which each sample was collected with the object of noting whether the accessories show any changes in character between the highest and lowest parts of the granites exposed. The pneumatolytic minerals are those most likely to be affected, and their probable irregular distribution has been commented on:

(ii) By A. K. Wells (1931) who claims that these minerals will be most abundant in the higher parts of an intrusion where the fluxes are concentrated.

(ii) By R. W. Marsden (1935) who suggests that these minerals will only occur where the fugitive constituents of the magma are unable to escape. Consequently they will be present in the lower parts of the intrusion, but absent from the higher regions where the fluxes were able to escape into the overlying roof.

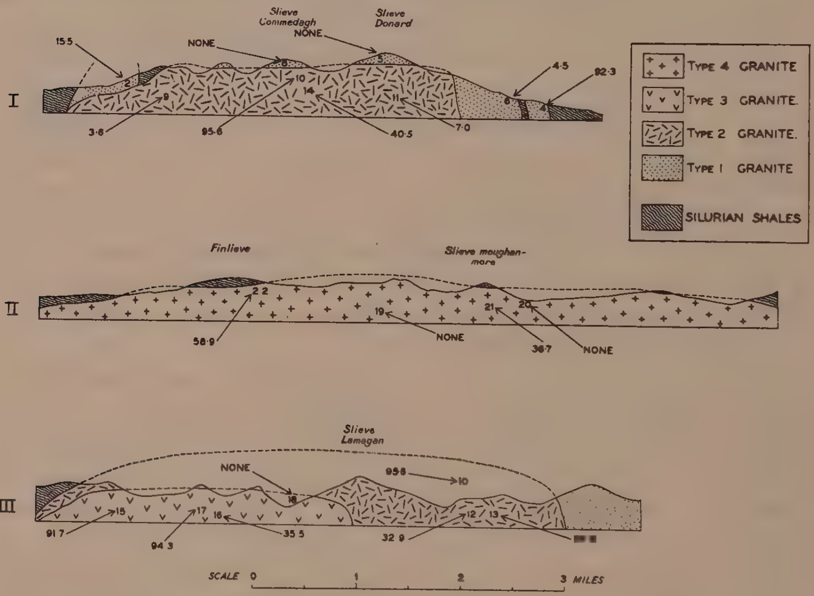

FIG. 2. Distribution of fluorite in the Mourne Mountains granites.

In any granite mass it is not the actual height from which the various specimens were collected that is significant, but their relative distances from wall and roof-rock. Of the two, the latter is the more important: but in granites which have been completely un-roofed it must remain an unknown factor. In the Mourne Mountains, however, not only are there preserved a number of roof-pendants of shale, but also we have remnants of the earlier granites forming the roof into which the later granites were intruded. The complex is, therefore, a particularly suitable one for an investigation of the effect of proximity to roof-rock on the pneumatolytic minerals.

In Fig. 2 the author has reproduced three of the sections across the Mountains given by Richey, and has superimposed on them the numbers of nineteen out of the twenty-two samples examined, together with the percentage of fluorite present in each case. Samples collected from points off the lines of section have been, where possible, projected onto the sections at the correct height.

In Section 1 it will be seen that Samples 5, 8 and 2 collected from near the floor of the Type 1 granite yield in two cases no fluorite and in the third only 15.5 per cent (of the non-magnetic heavy accessories). Sample 4, near the junction of this granite with the shale roof yields 92.3 per cent, while Sample 6 further from the contact yields only 4.5 per cent. In the Type 2 granite, Sample 10 with 95.6 per cent, fluorite is close beneath the roof of Type 1 granite capping Sleive Commedagh, while Samples 14, 11 and 9 at successively greater distances from the roof yield 40.5 per cent, 7.0 per cent and no fluorite respectively.

In Section 2 the figures for the Type 4 granite show that Samples 22 and 21 with 58.9 per cent and 36.7 per cent of fluorite respectively are in close proximity to roof-pendants of shale, while Samples 19 and 20, further removed from these pendants, yield no fluorite.

In Section 3 the results are less conclusive. In the Type 2 granite Samples 12 and 13 which are well removed from the roof of the intrusion yield 32.9 and 84.8 per cent of fluorite respectively. Samples 17, 15 and 16 of the Type 3 granite which are at successively greater depths below the roof yield normal descending percentages—94.3, 91.7 and 35.5, but Sample 18, which is in close proximity to the roof and might be expected to be rich in fluorite, is quite devoid of the mineral.

Taken by and large, however, the results for fluorite appear to bear out Wells' contention that the pneumatolytic accessories tend to be concentrated in the higher parts of an intrusion. Unfortunately in the Mourne Mountains complex, pneumatolytic minerals other than fluorites are present in such minute quantities that no conclusions can be drawn from their distribution.[1]

Brammal (in Groves, 1930) has found that on Dartmoor, there is some slight difference in habit between the zircons of the highest and lowest portions of the granite exposed, and it might be expected that a similar state of affairs would obtain in the Mourne Mountains. It has been established by experimental work on the crystallisation of salts that the habit of the crystals can be varied by controlling the physical conditions under which they form. It is not unreasonable, therefore, to assume that the same general statement should be true of rock-forming minerals, not excepting the accessories that form at high magnetic temperatures. The differences of crystal development are very real, and in the present state of our knowledge there is no other known set of factors that could control habit but physical conditions or chemical variations in the environment of the growing crystals.

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[1] The minerals beryl and topaz, which are well developed in drusy cavities, are absent or very rare as true accessories in the granites.

Since the highest and lowest exposures of granite in the Mourne Mountains are separated by rather more than 2000 feet, the complex appears to be well suited to demonstrate the influence of at least one of these factors upon the crystal habit of the zircons: complications, however, are introduced by the presence of four distinct intrusions each of which be considered separately—and the rather unusual form of these intrusions. The samples of Types 2, 3 and 4 can be dealt with in a standard manner, treating each type separately and calculating the average percentage of each variety of zircon present in three "height zones."[2] The three zones, selected with regard to the various heights from which specimens were available are as follows:—

(1) 500′–800′ (2) 900′–1200′ (3) 1300′ upwards

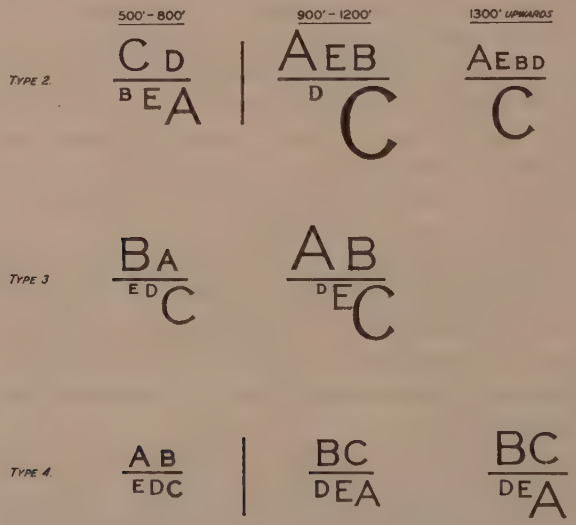

FIG. 3. Diagrammatic representation of variation of zircon in the Mourne Mountains granites.

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[2] The form of the Type 1 granite intrusion makes it impossible to apply the same treatment to it.

For each of these three height zones the average percentage of the five types of zircon in Table 3 has been calculated and also the positive or negative deviation from the average for the whole complex. The results are represented diagrammatically in Fig. 3. For each height zone[3] a symbol is given in which *A*, *B*, *C*, *D* and *E* indicate the five varieties of zircon. Above a central horizontal line are placed the letters corresponding to the types of zircon which have a percentage above the average for the whole complex: below the line are the letters corresponding to the types which are below the average. The type which is most above the average is placed at the left above the line, and the type most below the average at the right below the line: while the size of the letters used gives some indication of the relative surplus or deficit of each type. Set out in this manner certain facts are immediately obvious.

In the Type 2 granite the symbols for the two higher zones are very similar (the only difference being a slight deficit of *D* in one zone and a slight surplus in the other), but are markedly different from the symbol for the lowest zone: in the Type 4 granite exactly the same occurs. It is noteworthy that in both cases the type of zircon which is most above the average in the lowest zone is also most below the average in the other two zones. It, therefore, appears that in these two types of granite there is a noticeable difference in the character of the zircon above and below the 400′ level.

In the Type 3 granite the symbols for the two lower zones (the only ones available) are very similar. If there is any change in the character of the zircon of this intrusion it occurs either below the 500 foot level or above 1200 feet. It is not, of course, to be expected that variation of the zircon in the three types will be apparent at the same altitude since each type was intruded separately and at a different level.

It appears, therefore, that in the two intrusions most suitable for an investigation, there is quite an appreciable change in the character of the zircon between the highest and lowest samples collected. It must be remembered that in neither case was the vertical range more than 1000 feet and consequently one feels that in the comparison of separate but co-magnetic granites which have been eroded to levels differing by several thousand feet—as may frequently be the case—there are liable to be major differences in the habits of the zircons from the separate masses. In fact as Wells (1931) has expressed it: "The Dartmoor type of zircon, if it exists, may well give place in depth to the St. Austell type."

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[3] Owing to the low ground occupied by the Type 3 granite, none of the samples from it falls in the third zone—1400′ upwards.

## SUMMARY AND CONCLUSIONS

Methods of separating the heavy accessory minerals of igneous rocks are discussed and the necessity of using quantitative methods stressed.

From a consideration of the Mourne Mountains granite complex it is evident that the degree of variation between the accessory mineral suites from the four intrusions is of the same order as the variation between different samples of any one of the intrusions, both as regards the occurrence of mineral species and their varietal characteristics.

Both the nature of the zircon and the quantity of the fluorite present appear to be affected to a considerable degree by the distance from the roof of the intrusion and consequently before using these minerals as a basis for correlation of two or more granites one must be satisfied that one is sampling approximately the same level in the different masses.

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TABLE 1. HEAVY ACCESSORY MINERALS FROM THE MOURNE MOUNTAINS GRANITES

| | | | | Normal accessories | | | | | | | | | Pneumatolytic accessories | | | | | Secondary accessories | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Approx. Altitude (feet) | Index Figure | Biotite | Hornblende | Zircon | Apatite | Sphene | Pyrrhotite | Magnetite | Ilmenite | Orthite | Anatase | Rutile | Tourmaline | Topaz | Fluorite | Chlorite | Epidote | Zoisite | Clinozoisite | Limonite | White Mica | Haematite |
| Sample | 1 | 1800 | 2.5 | x | x | x | x | | | x | x | | | x | | x | x | x | x | | | x | x | |
| Outer | 2 | 1400 | 3.7 | x | x | x | x | | | | x | x | | | x | | x | x | | | | | x | |
| | 3 | 1000 | 0.8 | x | | x | | | | | x | | | | | | x | x | | | | x | | x |
| | 4 | 600 | 0.3 | x | | x | | | | x | | x | | x | | | x | x | | | | x | x | x |
| Type I | | | | | | | | | | | | | | | | | | | | | | | | |
| | 5 | 2700 | 7.3 | x | x | x | x | x | | x | | x | | | x | | | | | x | | x | | |
| Inner | 6 | 900 | 1.3 | x | | x | | x | | x | x | | | | | | x | x | x | | | | x | x |
| | 7 | 800 | 2.4 | x | | x | x | | | | x | | | x | | | x | x | x | | | | x | x |
| | 8 | 2000 | 1.4 | x | x | x | | | | | x | | | | | | | x | | | | | x | x |
| | 9 | 1200 | 1.5 | x | | x | | | x | | x | | | | | x | | x | x | | | x | x | x |
| | 10 | 1900 | 2.1 | x | | x | | | | | x | | | | | | x | x | x | | | x | x | x |
| Type II | 11 | 1300 | 2.0 | x | | x | | | | | x | x | | | | x | x | x | x | | | x | x | x |
| | 12 | 700 | 4.5 | x | | x | x | x | | x | x | | | x | | | x | x | x | | | x | | |
| | 13 | 600 | 2.0 | x | | x | x | x | | x | | x | | x | | | x | x | | | | | | x |
| | 14 | 1400 | 3.1 | x | | x | | x | | x | | | | | | | x | x | x | | | x | x | |
| | 15 | 700 | 0.8 | x | | x | | x | | x | | | | | | | x | x | x | | | | | x |
| Type III | 16 | 500 | 2.1 | | | x | | x | | x | | | | | | | x | x | x | | x | | x | |
| | 17 | 900 | 2.1 | x | | x | | | | | x | | x | | | | x | x | | | | | x | x |
| | 18 | 1100 | 0.6 | x | | x | | x | | x | x | x | | | | | | x | | | | x | x | |
| | 19 | 600 | 3.0 | x | x | x | x | x | | | x | x | | | | | | x | x | | | x | | |
| Type IV | 20 | 1000 | 1.0 | x | | x | x | x | | | x | x | | | | | | x | x | | | x | x | x |
| | 21 | 900 | 1.3 | x | | x | x | x | | x | x | | | | | | x | | x | | | | | x |
| | 22 | 1600 | 2.5 | x | | x | x | | | x | | | | | x | | x | x | x | | x | x | | x |

TABLE 2. PERCENTAGES OF NON-MAGNETIC ACCESSORIES FROM THE MOURNE MOUNTAINS GRANITES

| | | | Approx. Altitude (feet) | Index Figure | Normal accessories | | | | Pneumatolytic accessories | | | | | Secondary accessories | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Zircon | Apatite | Sphene | Orthite | Anatase | Rutile | Tourmaline | Topaz | Fluorite | Epidote | Zoisite | Clinozoisite | White Mica |
| Type I | Outer | Sample 1 | 1800 | 2.5 | 18.7 | 3.0 | | | | 1.0 | | 2.0 | 47.6 | 1.7 | | | 26.0 |
| | | 2 | 1400 | 3.7 | 68.4 | 10.2 | | 0.9 | | | 0.5 | | 15.5 | | | | 4.5 |
| | | 3 | 1000 | 0.8 | 11.4 | | | | | | | | 88.6 | | | | |
| | | 4 | 600 | 0.3 | 3.9 | | | 2.3 | | 0.3 | | | 92.3 | | | | 1.2 |
| | Inner | 5 | 2700 | 7.3 | 36.2 | 12.8 | 47.4 | 1.5 | | | 1.0 | | | | 1.1 | | |
| | | 6 | 900 | 1.3 | 73.5 | | 2.9 | | | | | | 4.5 | 14.7 | | | 4.4 |
| | | 7 | 800 | 2.4 | 11.1 | 0.8 | | | | 0.1 | | | 87.1 | 0.5 | | | 0.4 |
| | | 8 | 2000 | 1.4 | 97.7 | | | | | | | | | | | | 2.3 |
| Type II | | 9 | 1200 | 1.5 | 91.8 | | | | | | | 3.6 | | 3.2 | | | 1.4 |
| | | 10 | 1900 | 2.1 | 3.5 | | | | | | | | 95.6 | 0.3 | | | 0.6 |
| | | 11 | 1300 | 2.0 | 56.7 | | | 1.9 | | | | 3.8 | 7.0 | 4.5 | | | 26.1 |
| | | 12 | 700 | 4.5 | 46.6 | 10.5 | 4.1 | | | 0.9 | | | 32.9 | 5.0 | | | |
| | | 13 | 600 | 2.0 | 13.6 | 0.3 | 1.0 | 0.1 | | 0.2 | | | 84.8 | | | | |
| | | 14 | 1400 | 3.1 | 31.3 | | 11.7 | | | | | | 40.5 | 9.0 | | | 7.5 |
| Type III | | 15 | 700 | 0.8 | 6.7 | | 0.9 | | | | | | 91.7 | 0.7 | | | |
| | | 16 | 500 | 2.1 | 6.6 | | 41.1 | | | | | | 35.5 | 9.7 | | 1.2 | 5.9 |
| | | 17 | 900 | 2.1 | 2.4 | | | | 0.4 | | | | 94.3 | | | | 2.9 |
| | | 18 | 1100 | 0.6 | 10.8 | | 3.2 | 0.5 | | | | | | | | | 85.5 |
| Type IV | | 19 | 600 | 3.0 | 68.6 | 5.2 | 8.7 | 9.3 | | | | | | 8.1 | | | |
| | | 20 | 1000 | 1.0 | 88.3 | | 3.6 | 2.5 | | | | | | 4.1 | | | 1.5 |
| | | 21 | 900 | 1.3 | 30.2 | 2.3 | 3.9 | | | | | | 36.7 | 25.6 | | | 1.3 |
| | | 22 | 1600 | 2.5 | 15.1 | 1.0 | | | | | 1.2 | | 58.9 | 19.5 | | 4.3 | |

TABLE 3. QUANTITATIVE DATA OF ZIRCON AND APATITE FROM THE MOURNE MOUNTAINS GRANITES

| | | Approx. Altitude (feet) | Index Figure | Zircon | | | | | Apatite | | | Ratio anhedral: euhedral apatite | Ratio apatite: zircon |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | (a) Equi-dimensional | (b) Stout | (c) Medium elongated | (d) Much elongated | (e) Anhedral | (a) Stout prismatic | (b) Needle-shaped | (c) Anhedral | | |
| Type I, Outer | Sample 1 | 1800 | 2.5 | 2.8 | 19.4 | 61.2 | 2.7 | 13.9 | 50.7 | | 49.3 | 1:1 | 1:6 |
| | 2 | 1400 | 3.7 | 5.1 | 30.9 | 48.3 | | 15.7 | 42.9 | | 57.1 | 4:3 | 1:7 |
| | 3 | 1000 | 0.8 | 15.7 | 23.9 | 48.1 | | 12.3 | | | | | |
| | 4 | 600 | 0.3 | | 12.5 | 49.8 | | 37.7 | | | | | |
| Type I, Inner | 5 | 2700 | 7.3 | 2.2 | 15.4 | 68.1 | 14.3 | | 32.5 | | 67.5 | 2:1 | 1:3 |
| | 6 | 900 | 1.3 | 14.8 | 35.2 | 31.5 | | 18.5 | | | | | |
| | 7 | 800 | 2.4 | 7.7 | 21.5 | 58.5 | 6.1 | 6.2 | 40.8 | | 59.2 | 3:2 | 1:14 |
| | 8 | 2000 | 1.4 | 32.5 | 41.1 | 1.1 | | 25.3 | | | | | |
| Type II | 9 | 1200 | 1.5 | 26.1 | 39.9 | 12.3 | | 21.7 | | | | | |
| | 10 | 1900 | 2.1 | 17.9 | 27.5 | 27.2 | 9.1 | 18.3 | | | | | |
| | 11 | 1300 | 2.0 | 30.3 | 42.7 | 14.6 | 4.5 | 7.9 | | | | | |
| | 12 | 700 | 4.5 | 2.3 | 22.1 | 51.2 | 9.3 | 15.1 | 55.6 | | 44.4 | 3:4 | 1:4 |
| | 13 | 600 | 2.0 | 7.2 | 40.6 | 37.7 | 8.7 | 5.8 | 52.1 | | 47.9 | 1:1 | 1:45 |
| | 14 | 1400 | 3.1 | 14.4 | 35.4 | 20.5 | | 29.7 | | | | | |
| Type III | 15 | 700 | 0.8 | 13.6 | 31.8 | 38.6 | 2.3 | 13.7 | | | | | |
| | 16 | 500 | 2.1 | 25.9 | 51.9 | 7.4 | | 14.8 | | | | | |
| | 17 | 900 | 2.1 | 21.4 | 46.4 | 25.0 | | 7.2 | | | | | |
| | 18 | 1100 | 0.6 | 34.9 | 36.5 | 14.3 | 4.8 | 9.5 | | | | | |
| Type IV | 19 | 600 | 3.0 | 19.3 | 36.4 | 31.8 | | 12.5 | 55.4 | | 44.6 | 3:4 | 1:13 |
| | 20 | 1000 | 1.0 | 13.8 | 39.7 | 37.9 | | 8.6 | | | | | |
| | 21 | 900 | 1.3 | 1.7 | 41.4 | 44.8 | | 12.1 | 61.7 | | 38.3 | 5:8 | 1:13 |
| | 22 | 1600 | 2.5 | 3.1 | 42.3 | 43.7 | | 10.9 | 83.3 | | 16.7 | 1:5 | 1:15 |

Table 4. Comparison of the Accessory Mineral Suites of the Four Types of Granite from the Mourne Mountains

| | Type I | Type II | Type III | Type IV |
|---|---|---|---|---|
| 1. Average Index Figure | 2.5 | 2.5 | 1.4 | 2.0 |
| 2. Hornblende | Present in half the samples. | Absent. | Absent. | Present in a quarter of the samples. |
| 3. Zircon | Percentage present 40.1%. Medium elongated type dominant—Samples 6 & 8 exceptions. | Percentage present 40.6%. Stout type dominant—Sample 12 an exception. | Percentage present 6.6%. Stout type dominant—Sample 15 an exception. | Percentage present 50.5%. Stout and medium elongated varieties in approximate equal proportions dominant. |
| 4. Apatite | Present in half the samples. Anhedral crystals dominant over euhedral. | Present in one-third of the samples. | Absent. | Present in three-quarters of the samples. Euhedral crystals dominant over anhedral. |
| 5. Sphene | Present in a quarter of the samples. | Present in half the samples. | Present in three-quarters of the samples. | Present in three-quarters of the samples. |
| 6. Pneumatolytic Minerals | Reasonably well represented. One member present in most samples. | Well represented. At least one member present in each sample. | Represented only by fluorite. | Poorly represented. Only present in half the samples. |
| 7. Epidote | Poorly represented. Present in half the samples only. | Well represented. Present in five-sixths of the samples. | Poorly represented. Present in half the samples only. | Very well represented. Present in every sample. |

# VEIN QUARTZ PSEUDOMORPHS OF CROSS-FIBER ASBESTOS IN VIRGINIA

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## Contents

Introduction . . . . . 701
- The Fibrous Habit . . . . . 701
- Fibrous Quartz a Rare Phenomenon? . . . . . 703
- Significance of Fibrous Quartz Veins in Virginia . . . . . 705

The Virginia Deposits . . . . . 707
- Distribution, Size and Character of the Veins . . . . . 707
- Nature of the Wallrocks . . . . . 709
- Replacement Origin of the Original Asbestos Veins . . . . . 710
- Character of the Pseudomorphous Quartz . . . . . 711
- Evidences of Secondary Introduction and Replacement Origin of the Fibrous Quartz . . . . . 713
- Non-fibrous Quartz of Secondary Introduction and Replacement Origin . . . . . 713

Some Problems . . . . . 714
- Origin of the Asbestos Veins . . . . . 714
- Cause of the Fibrous Structure . . . . . 715
- Possible Influence of Subjacent Intrusives on the Origin of the Fibrous Quartz . . . 716

Summary . . . . . 717

Acknowledgments . . . . . 719

References . . . . . 719

## Introduction

*The Fibrous Habit.* In addition to the asbestos of commerce, which includes several varieties of amphibole and serpentine, many minerals occur in the asbestiform or fibrous habit, a few much more commonly than others. Dana (1922, p. 690) records more than forty such minerals, and states (p. 182) that "there are many gradations between coarse columnar and fine fibrous structures." This implies that any mineral which develops a columnar form during primary crystallization might assume a fibrous habit under certain conditions. Peacock (1928, p. 276) points out that the beginnings of crystallization in amorphous media and hydrogels are commonly fibrous crystallites which may finally develop into non-fibrous crystals. This observation leaves Taber's statement (1916A, p. 659), that all asbestiform minerals are secondary and, therefore, limited to metamorphic rocks, open to question. Both these writers agree, however, that because all fibrous minerals also show well-developed crystals, their fibrous structure must be due to special conditions of growth.

Warren (1932) demonstrates that the tendency to form somewhat flexible and extremely elongated crystals is inherent in the molecular pattern of some minerals, especially certain varieties of asbestos. In other words, a few minerals adopt an asbestiform outline very readily in response to intramolecular forces peculiar to them. This is not true of the great majority of minerals. Consequently, their appearance in fibrous form must be a result of conditions outside the space-lattice.

Numerous examples are known of a fibrous habit among minerals to which this habit is inherently foreign. Most of these are vein occurrences in which fibers of a rarely-fibrous mineral are inter-grown with one or more commonly-fibrous ones, and explanations proposed to account for specific instances of this circumstance have been:

A. Infiltration—in which either (1) the minerals crystallized simultaneously, one of them attaining the fibrous condition because it occupied and was moulded by space between growing fibers or bundles of fibers of the other; or (2) later solutions permeated an asbestiform vein and deposited material whose form was determined by space it secured through displacement (of fibrous masses), just as the shape of a dike or vein is often controlled by the walls of the fracture along which it has penetrated. Renard and Klement (1884), Hall (1918A, p. 35), Peacock (1928, p. 247) and Reinecke and McClure (1933, p. 31) have described examples of minerals made fibrous through infiltration, but only Renard and Klement are very definite in stating that the infiltration did not result in replacement.

B. Pseudomorphism—in which the asbestiform structure is inherited through replacement. It is conceivable that in this process one fiber of palasome may be succeeded by one (fiber) of metasome—that is, that the new fibers are *unit* pseudomorphs. Usually, however, the replacement proceeds *en masse*, whole bundles of fibers giving rise to much coarser fibers of the replacing substance—that is, the new fibers are *aggregate* pseudomorphs. Klaproth (1815) and Wibel (1873) conclude that coarse fibers of quartz in the famous tiger-eye of South Africa are aggregate pseudomorphs of the crocidolite with which they are intergrown. E. L. Perry (1930) describes fibrous magnetite pseudomorphs of chrysotile from Wyoming in which (p. 178) "only the coarser structure of the [chrysotile] fibers (0.1 mm.) is preserved." This, likewise, is obviously an example of aggregate pseudomorphism; and numerous others could be cited. No instance of unit pseudomorphism among fibrous minerals has yet come to the writer's attention, but, as noted above, no *a priori* reason precludes the possibility of its occurrence.

Since metasomatism is frequently a highly selective process, influenced by minute and little-understood physico-chemical differences in the material suffering attack, all gradations may exist between unit pseudomorphs which inherit microscopic details of the fibers they replace and coarse aggregate pseudomorphs which preserve only the major outlines and structural features of fiber bundles, or even of entire fibrous veins.

Petrified wood presents an analogous variability in the intricacy of original structures retained. Furthermore, since all stages of replacement from incipient to complete are possible in any instance, residual fibers may or may not be present in all proportions within such aggregate pseudomorphs. Consequently, material having a decidedly fibrous aspect in the field and in hand specimens may appear as a granular mosaic of non-fibrous units in thin section. Because of this it is well to bring into clearer focus what the geologist has in mind when using the terms *fiber* and *fibrous*.

Dana (1922, p. 182) says, "The structure . . . is called *fibrous* when the mineral is made up of fibres, as in asbestus, also the satin-spar variety of gypsum." Precise limits to the dimensions of a fiber have not been established, and would be purely arbitrary inasmuch as fibrous forms grade into columnar ones. A fiber of inorganic substance may consist of: a single, imperfectly crystallized and much elongated crystal, a series of such individuals placed end to end, a series of unelongated crystalline grains or plates whose lateral dimensions (i.e. normal to the fiber length) are equivalent, or a single threadlike mass of glass or amorphous material. Strict adherence to Dana's rigid definition of *fibrous structure* would prevent us from applying the term to the aggregate pseudomorphs described above, in which there are no individual fiber units.

*Fibrous Quartz a Rare Phenomenon?* Quartz has been considered among the minerals to which the fibrous habit is abnormal and, therefore, of uncommon occurrence. Fibrous quartz has been known for more than a century, and there are divers references to it in the literature of geology. Most of these, however, are descriptions of the same few instances by writers who disagree on the nature and origin of the fibrous structure. The first discovery of fibrous quartz is attributed by Hintze (1897, p. 1265) to Klaproth (1815) who believed, as noted above, that the quartz; of the African tiger-eye forms aggregate pseudomorphs of the associated crocidolite. Wibel (1873) supports this conclusion; Renard and Klement (1884) describe the occurrence without discussing the origin of the quartz; Hall (1918B) speaks of "infiltrated quartz" (p. 23), but does not specify whether infiltration involved replacement or displacement; and Peacock (1928, p. 247), from his study of material collected by Palache in Africa during 1922, says, "Although it might be held that the fibrous quartz . . . has replaced fibrous asbestos, the impression gained from the sections is that the two minerals grew concurrently"—that is, that the quartz was *moulded* by the contiguous asbestos. A similar controversy has occurred over fibrous quartz in Massachusetts and Rhode Island. Although the authorities agree thus far that each deposit described represents quartz developed through pseudomorphism (which appears to be of the aggregate type), they disagree about the identification of the palasome mineral. Emerson (1917, p. 63) holds that fibrous quartz in veins in phyllite near Worcester, Massachusetts (described previously by J. H. Perry and Emerson, 1903, p. 17) and in veins in the western part of the Narragansett Basin replaced "a prochlorite, possibly made fibrous by pressure"—a very uninformative statement. Hawkins (1918) concludes from extinction angles and color that the original mineral in veins of fibrous quartz in Carboniferous sediments near Providence, R. I., was actinolite asbestos. Richards' (1925) study of the same occurrence reveals that the wallrocks are graphitic schists and that the quartz replaced aphrosiderite.

The conglomerates of the auriferous Witwatersrand are known to contain fibrous quartz of secondary origin. I. Thord-Gray (1905, p. 72) refers to it as "honeycomb quartz with a very minutely fibrous structure"; Young (1907, p. 18) calls it a "fibrous form of secondary silica" which he later (1914, pp. 31–38) terms "fibrous quartz"—specifying still later (1917, p. 42) that it is the "infilling of a cavity" between secondary pyrite nodules (pseudomorphs of detrital quartz grains) and secondary massive quartz. No mention is made of an associated or preexisting fibrous mineral in this example of fibrous quartz. Young does record a radially-fibrous structure in some of the pyrite (1917, p. 65), but it is clear that the quartz has neither replaced this structure nor been molded by it. This, then, seems to be an illustration of a secondary, fibrous mineral which, apparently, achieved its unusual form free from the influence of another. Two other examples of the same type of phenomenon—that is, quartz made fibrous through some as yet obscure conditions attending its independent growth, deserve notice here as samples of what, the writer suspects, will eventually be found of common occurrence. (1) Howchin (1912, p. 197) notes veins of fibrous quartz traversing boulders of quartzite in the Permo-Carboniferous tillite of Australia. He does not describe the veins or discuss their origin, but no associated fibrous mineral is specified. (2) The writer recently found a vein of fibrous quartz with no associated asbestiform material in a boulder of quartzitic arkose within the Squantum tillite at Squantum, Mass.

Within recent months several additional cases of fibrous quartz which either grew concurrently with, filtered into and displaced, or replaced asbestiform amphibole have come to the writer's attention, viz.: in coarse veins from Wyoming (W. De Laguna);[1] in metamorphosed volcanic rocks at Newton Upper Falls, Mass. (Dr. M. P. Billings); in femic dikes within the Roxbury conglomerate in Boston, Mass. (B. F. Buie) and in Chestnut Hill, Mass. (R. W. Sayles); in the Brighton Melaphyre in Allston, Mass. (L. R. Thiesmeyer); in basic volcanics in Dover, Mass. (R. F. Wiggins and R. A. Chandler); and in an altered Pre-Cambrian granite in Virginia (L. R. Thiesmeyer).

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[1] Names in parentheses indicate persons who discovered these examples and have discussed them with the writer. Details and conclusions concerning them will be published eventually by those named or by the writer.

From a consideration of the remarks above, several generalizations may be made concerning fibrous quartz:

(A) Its occurrence is not limited to any particular type of rock, geological horizon, obvious mineral association, or geographic position.
(B) It is not always clearly associated with an asbestiform mineral in origin.
(C) It is, apparently, always a secondary mineral.

Further investigation of known occurrences and of new ones may disprove these statements, but, to the writer's knowledge, they stand at present unchallenged.

From (A) it follows that fibrous quartz may be expected almost anywhere. However, because there may be confusion about the application of the term *fibrous*, and because (except to the economic geologist) quartz veins are often easily-overlooked, incidental features of the rocks which contain them, references to fibrous quartz are scattered and relatively few. Nevertheless, the writer believes that fibrous varieties of quartz are far more common than has been supposed. One aim in offering this paper is to summarize the present state of knowledge regarding a feature which, regardless of the frequency or rarity of its existence, always requires special explanation. By thus focusing attention upon it, the writer hopes to stimulate the search for further illustrations of fibrous quartz which may confirm or disprove the suggestion just made.[2]

*Significance of Fibrous Quartz Veins in Virginia.* The presence of amphibole asbestos seams in the Catoctin greenstones of the northern Piedmont and Blue Ridge was recorded for Virginia long ago by Rogers (1884) and confirmed by Keith (1894) and others. Stose and Bascom (1929, p. 5) report them in Pennsylvania, and Furcron (1934, p. 402) notes "green, fibrous asbestos and quartz" in the Shenandoah National Park area. Furcron does not describe this material or state clearly whether the quartz is also fibrous; but Thiesmeyer (1936, p. 198) calls attention to fibrous quartz representing all stages of replacement and aggregate pseudomorphism of similar amphibole asbestos seams in the Blue Ridge of northwestern Fauquier County, Va., a few miles northeast of the area studied by Furcron. Further study of this material and of the geology of Fauquier County has disclosed: (1) that such seams are widely distributed through the Catoctin greenstones in this vicinity (Fig. 1); (2) that the asbestos seams are chiefly cross-fiber actinolite—which Merrill (1896) and Taber (1917, p. 84) consider rare; (3) that the veins of cross-fiber quartz range up to $2\frac{1}{2}$ feet wide (Fig. 2)—which makes them the largest veins of fibrous quartz yet described; (4) that the original actinolite seams clearly developed by replacement of the wallrock rather than by pushing it aside through the pressure of growing crystals, as Taber (1917) claims is true of most asbestiform veins; and (5) that this example of fibrous quartz represents an indubitable case of pseudomorphism rather than concurrent growth or infiltration without replacement. In addition to the regional character of the fibrous quartz in Virginia, these generalizations deserve proof through a more detailed description of the material here. This may help to clarify the nature and

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[2] The writer will welcome criticism of this paper, information regarding new occurrences, references which may have escaped his attention, and especially specimens of fibrous quartz to augment his small collection.

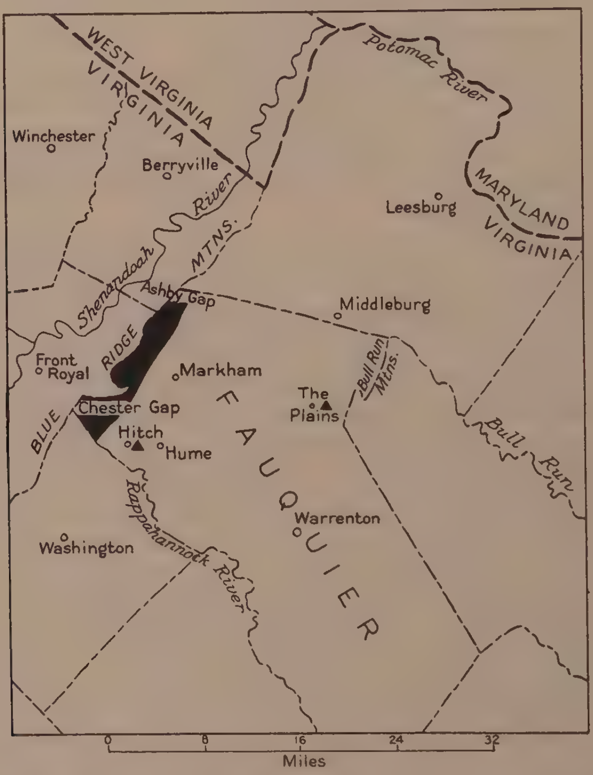
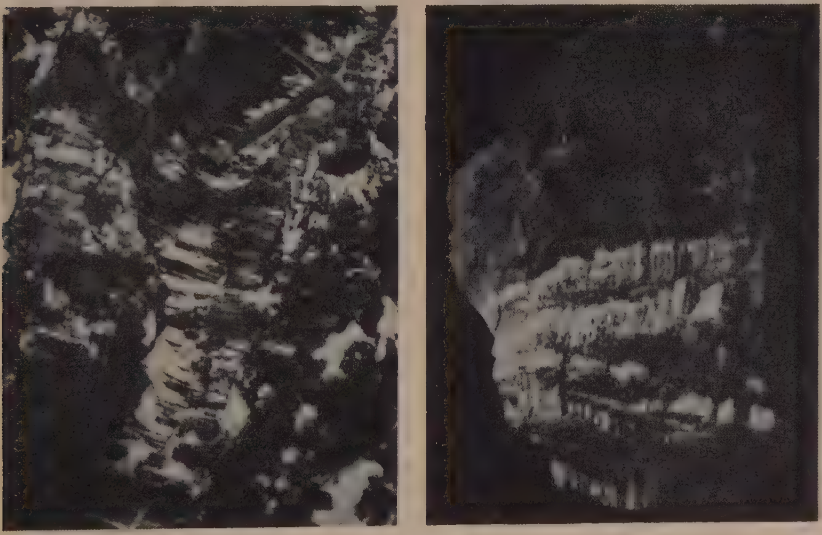


FIG. 1—Sketch map of northern Virginia, showing location of Fauquier County and districts in which fibrous quartz is abundant (black).

origin of other occurrences of fibrous quartz, and point the direction of emphasis in their investigation.

## THE VIRGINIA DEPOSITS

*Distribution, Size and Character of the Veins.* Traverses along and across the belt of Catoctin greenstones which cap the Blue Ridge in Fauquier County, Virginia, disclosed literally thousands of lenticular seams of cross-fiber actinolite asbestos in all stages of replacement by transparent to milky quartz. These were found at irregular intervals all the way from Ashby Gap to Chester Gap, a distance of about thirteen miles. Similar veins were found in metabasalt dikes intruding gneissose granites between Hitch and Hume; and still others were noted a half mile east of the Plains in Catoctin greenstones which comprise a broad belt just west of the Bull Run Mountains. This latter exposure is more than twelve miles east of the Blue Ridge occurrences. It is entirely possible that many examples of such veins were overlooked by the writer throughout northwestern Fauquier County before his curiosity was stimulated by their profusion and magnitude in the Ridge country, and that they are an even more characteristic feature of certain facies of the Catoctin greenstones than is thus far suggested. At any rate, their distribution, as



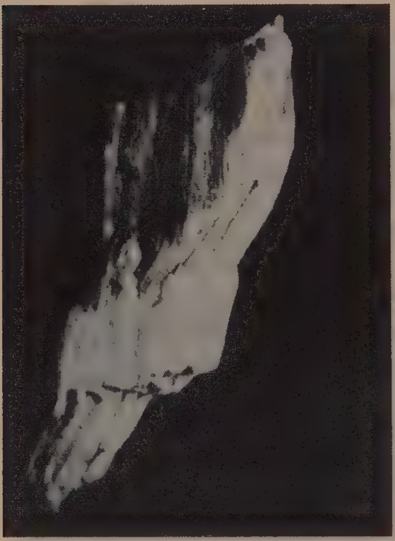
(FIG. 2*a*) (FIG. 2*b*)

FIG. 2—(*a*) The largest known vein of fibrous quartz in the world. Snow serves to accentuate the fibrous appearance. 4 miles northwest of Markham, Va.

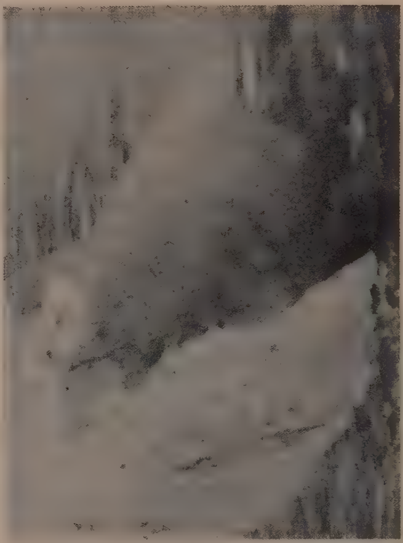
FIG. 2—(*b*) Boulder of Catoctin greenstone from the Blue Ridge, containing quartz pseudomorphs of cross-fiber actinolite veins up to 2 inches wide.

indicated in Fig. 1, shows that they are of regional rather than local importance.

These veins range from almost microscopic, hairlike films up to 2½ feet wide (Fig. 2*a*) and are arranged in subparallel groups which bear a somewhat en echelon relationship. Single boulders little more than a foot in diameter may contain dozens of them (Fig. 2*b*). Though the veins appear over many square miles of territory, as units they are small and local, ranging in length from a few millimeters to a few yards. Most of the veins are of the cross-fiber type (i.e., fibers oriented normal to the walls), but gradations to oblique fiber and to slip-fiber are common. Branching, bulging, bifurcation, central partings of wallrock of angular outline, monoclinal flexures—in fact, most of the features listed by Diller (1910), Taber (1924) and others as characteristic of asbestiform veins, are displayed in these Virginia deposits and have been inherited in varying detail by the pseudomorphous quartz which they contain (Fig. 3*a*).



(FIG. 3*a*)



(FIG. 3*b*)

FIG. 3—(*a*) Fibrous quartz pseudomorph of a monoclinal flexure developed through post-vein deformation of the original asbestos. ×1½.

FIG. 3—(*b*) Photomicrograph showing granulated mosaic of quartz, lacking asbestos inclusions, embedded in fibrous quartz crowded with residual asbestos. Nicols crossed. ×118.

About four miles northwest of Markham seams of a rather pure asbestos without fibrous quartz were found. They consist of dark-green, silky actinolite in bundles of readily-separable and inelastic fibers in which are embedded scattered aggregates of massive, opalescent to smoky, granulated quartz. Nearby veins of essentially the same character have numerous irregularly-spaced, fiber-like bands of quartz between the fiber-bundles, most of them only visible through a hand lens. Residual threads of actinolite which they enclose impart a greenish tinge to these quartz "fibers," the shade of green varying with the proportion of such material. These veins represent an incipient stage in the replacement of the asbestos veins by fibrous quartz. All stages of transition were found from veins of this type to those consisting of about 95% milky quartz (Figs. *2b*, *3a*), colored only locally by actinolite needles, and representing complete pseudomorphs of entire asbestos veins.

*Nature of the Wallrocks.* The Catoctin greenstones which contain these geological curiosities are a group of highly altered, volcanic rocks of basaltic affiliations which have been complexly folded, faulted and invaded by plutonic injections. Despite their involved history many remnants of original texture and structure suggest that these rocks were largely of extrusive character, and included flows, amygdaloids and pyroclastics. Keith (1894) described and named them and assigned them to the Pre-Cambrian. Recently Furcron and Woodward (1936) discovered that part of what had been mapped as Catoctin greenstone farther south is actually a basal Cambrian flow. Keith recognized two major subdivisions of the Catoctin, one invaded by granites, the other extrusive upon a floor of the same granites. Later workers have not followed this subdivision but have apparently regarded the Catoctin greenstones as a single unit of Pre-Cambrian volcanics, which some consider older and others declare younger than the adjacent granitic rocks. Incomplete studies by the writer suggest strongly that the Catoctin greenstones are divisible into a series of basaltic rocks whose eruption occurred periodically throughout late Pre-Cambrian and continued well into Lower Cambrian time.

Detailed descriptions of the Catoctin greenstones have been given by Keith (1894), Stose and Bascom (1929, p. 5), Furcron (1934) and others. The asbestos seams are present in massive, amygdaloidal, brecciated and highly schistose facies, but seem to be more common in the amygdaloids.

Thin sections of a moderately schistose wallrock from the Blue Ridge show its composition as: 20% feldspar (calcic oligoclase) in microlites arranged in somewhat ophitic pattern; 20% mosaic-textured quartz, most of which is secondary and is crowded with inclusions of the other minerals; 15% chlorite and epidote, the former oriented in a crude schistosity; 15% *actinolite in hairlike fibers having a random orientation, or in plumose, radiate groups;* 10% opaque oxide in subhedral, scattered grains; and 20% fine interstitial material of indeterminate nature (index and birefringence suggest carbonate for much of it). Of these constituents only the feldspar could be considered primary, the others having developed through metamorphism of what was probably an andesite or basalt. The amygdules consist of mosaics of anhedral quartz intergrown with subhedral to euhedral epidote. Both minerals enclose hairs of actinolite which often extend uninterrupted and undeformed across their mutual grain boundaries. Selvages of fibrous actinolite along the margins of the amygdules are invaded irregularly by the quartz filling. These relations indicate that the quartz and epidote of the amygdules formed later than and replaced former fillings of asbestos in some cases.

*Replacement Origin of the Original Asbestos Veins.* From a protracted study of asbestiform veins of many types, and from laboratory experiments in which he reproduced many of their essential features, Taber (1916A) concluded that most fibrous veins are the result of lateral secretion from the wallrocks, and that they make room for themselves by forcing their walls apart through the pressure exerted by the crystallization of their growing fibers. He agrees[3] with the writer, however, that this hypothesis is not applicable to the original asbestos veins of these Virginia deposits, which must have developed, rather, through replacement of the wallrocks. Proof of this is indicated in the relations outlined below.

No sign of even an incipient fracture was discernible beyond the ends of the veins; and no pressure effects within the wallrocks, or in adjacent veins which could be interpreted as results of forcible injection, or the wedging action of growing crystals, were discovered. The monoclinal flexures, gradation to slip-fiber and other irregularities, which Taber (1917, p. 83) would ordinarily attribute to differential movement of the walls during vein growth, are, in this case, clearly an effect of post-asbestos deformation because the individual fibers are shattered and strained. No sutures within the veins which might represent the original fracture that localized them, or might mark the boundary between fibers growing from opposite walls, were seen. Although macroscopically the vein walls appear very sharp, the vein material is not easily separable from the wall rock; and, in thin section under high power, the wall contact is a ragged border (with asbestos needles penetrating irregularly into the wallrock minerals) of the type attributed to replacement.

Several seams were located in a boulder northwest of Markham which afford striking megascopic proof of the replacement nature of the fibrous veins (Fig. 4). These consist of quartz pseudomorphs of actinolite seams.

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[3] Personal communication.

arranged, in this instance, normal to the schistosity of an epidotized flow. The amygdules have been elongated and flattened parallel to this foliation, and some of them have curious dumb-bell shapes where two have coalesced in a narrow bottle-neck. A few of the amygdules are embedded within the vein, others are partly in vein and partly in wallrock, while some extend completely across into wallrock on either side. Thus they are analogous to unsupported inclusions in a dike which has not disturbed their regional orientation in the least. Gradual replacement of the wallrock around them, so that at no time were they actually unsupported, seems the only satisfactory explanation of their unique relations. No fracturing could be seen in the amygdules within the vein, and they have not been attacked by either the original asbestos or the quartz which replaced it.

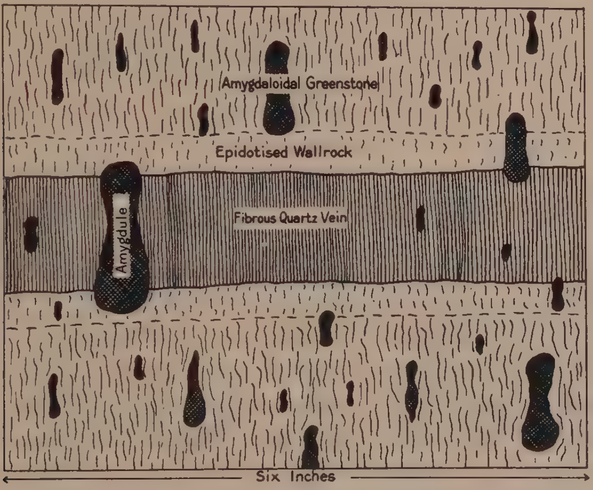

Fig. 4—Sketch of fibrous quartz seam enclosing amygdules whose orientation parallel to the schistosity has not been disturbed by replacement of the wallrock surrounding them.

*Character of the Pseudomorphous Quartz.* This fibrous quartz, unlike that described by Richards (1925), is not readily separable with the fingers, but does have a coarsely fibrous outline. A thin section cut parallel to the fiber-length was examined before it was completed, while still too thick for ordinary petrographic work. It showed masses 0.75 mm. wide by fifteen times as long which extinguished as units between crossed nicols. Upon slight warming of the balsam they could be separated longitudinally rather easily. However, when the section was ground to customary thinness, these units were seen to consist of a mosaic of smaller quartz grains—some elongated parallel to the thicker units, but many not elongated at all. They extinguished in all positions, indicating that the apparent unit extinction of the thicker mass is really the result of an overlapping of grains.

In transverse section the fibrous quartz appears as a mosaic of anhedral grains enclosing scores of residual actinolite fibers and sharing unreplaced bundles of them (Fig. 5). Delicately scalloped borders of these grains, revealed at high magnification, show that the quartz has inherited irregularly the transverse outlines of fiber-bundles. Out of 254 quartz grains measured with the Fedorov stage only $5\frac{1}{2}\%$ had their *c*-axes parallel to the fiber-length of the original asbestos, while the remainder were oriented at random. This indicates that the fibrous structure of the original vein had little influence on the orientation of the metacryst, even though its features were inherited in the aggregate. This was noted by Richards (1925), Reinecke and McClure (1933, p. 31) and Peacock (1928) in other examples of fibrous quartz. Peacock observes that the quartz fibers of the tiger-eye extinguish at all angles to their direction of elongation and says (p. 247), "It would thus seem that when quartz either replaces another fibrous mineral or grows concurrently with it, the elongation of the fibers is determined solely by the fortuitous orientation of the first quartz to crystallize, and is independent of the usual prismatic habit of quartz."

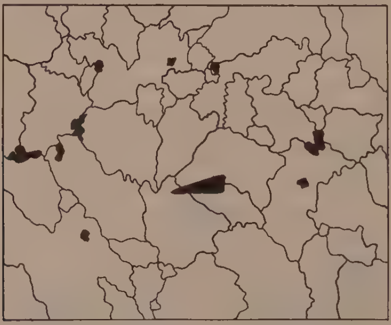

FIG. 5—Sketch made from a photomicrograph showing granular mosaic of quartz grains enclosing and sharing unreplaced bundles of actinolite (black). Section cut transverse to the fiber-length. Scalloped borders of the quartz suggest the outlines of asbestos bundles which it replaced. ×89.

In longitudinal section the fibrous quartz shows innumerable threads of included asbestos which extend uninterrupted across quartz-grain boundaries. The fibrous quartz is fractured and strained locally, but is not granulated or strained so severely as is the massive quartz of the original asbestos vein which occasionally appears in the midst of the pseudomorphous quartz (Fig. 3*b*).

Granular, secondary, subhedral to euhedral iron oxide scattered through the sections probably represents iron residue from the replacement process; while epidote concentrated along fractures within and traversing the quartz is obviously of later introduction.

*Evidences of Secondary Introduction and Replacement Origin of the Fibrous Quartz.* Proof that the fibrous quartz was not concurrent with the asbestos but was introduced after deformation of the latter is contained in the following facts:

A. The fibrous quartz shows none of the shattering and deformation common to the asbestos, but, on the contrary, encloses bent and broken residuals of it within the boundaries of a single grain.

B. Adjacent to veins which contain fibrous quartz the wallrock is thoroughly epidotized and silicified. The width of the zone of such alteration and its intensity are directly proportional to the amount of fibrous quartz present in the vein, and this alteration is totally absent along veins which lack this mineral. In other words, along with the introduction of quartz into the veins went the formation of quartz and epidote in the wallrock.

C. The features outlined below prove conclusively that, as has been already stated for the sake of clarity in description, the fibrous quartz is a secondary pseudomorph of the asbestos.

D. Actinolite inclusions are totally lacking in the original massive quartz of the veins, but are very abundant in the fibrous quartz, as noted above.

The universal absence of phenomena of displacement, varying in complexity with differing amounts of fibrous quartz present, argues strongly against any suggestion that the latter developed through pure infiltration without replacement. In addition to this negative evidence there is the positive evidence of replacement seen in thin sections, which show fibrous quartz invading bundles of actinolite laterally at several places and penetrating irregularly longitudinally from these points of attack, so that here only shreds of the bundles are left embedded in quartz, while farther along the same bundles are complete and unreplaced though surrounded by bundles which have suffered total replacement. Furthermore, the appearance in quartz of deformed structures like those of Fig. 3 is difficult if not impossible to explain except as an inheritance through replacement. Pressure great enough to have deformed the quartz plastically into such curious shapes would have left an indelible record of its operation in the wallrocks; indeed, it would probably have destroyed original minerals and textures.

*Non-fibrous Quartz of Secondary Introduction and Replacement Origin.* Poorly-defined veinlets with ragged margins which extend obliquely from the fibrous quartz veins into the wallrock can be seen in some thin sections. These consist of a mosaic of granular, massive quartz and epidote which preserves remnants of the textural pattern of the wallrock by enclosing ophitic feldspar laths, plumose groups of actinolite etc. Some of these included units are shared by adjacent grains of quartz or of quartz and epidote, and their original orientation has not been disturbed. Such veins are clearly developed by replacement, and their minerals are not granulated or strained. Presumably such veins were introduced contemporaneously with the fibrous quartz. Their lack of a fibrous character may be attributed to the absence of a uniform, well-oriented fibrous structure in the material which they replaced.

## Some Problems

*Origin of the Asbestos Veins.* The regional distribution of asbestos seams in this vicinity is a feature which demands explanation in terms of a cause or process of regional influence. Since fibrous amphibole, the dominant constituent of the veins, is almost universally present in the greenstones, it is reasonable to consider that the vein material developed at the same time and through operation of the same processes as those which produced the fibrous amphibole within the wallrock. Recrystallization of original pyroxene in the rock to produce the stellate, actinolite "mass-fiber" suggests that during metamorphism solutions of actinolitic composition, which might migrate into potential openings to form veins, were made available. Keith's statement (1894, p. 364) that the metamorphism of these rocks was "mainly chemical and has not affected the original proportions of the rock to a marked extent" strengthens such a postulate by indicating that the metamorphism was accomplished by reorganization of materials in situ without introduction of foreign material. According to Sederholm (1926, p. 131) such a condition invariably implies diffusion and interchange of solutions within the rock mass. Taber (1924, p. 482) notes that the minerals in cross-fiber veins are also commonly present in their wallrocks, and his hypothesis of a lateral secretion origin for such veins reveals that he conceives of essentially the circumstances just outlined. Apparently, however, the Virginia deposits are inharmonious with his statement (1917, p. 84) that asbestos minerals are "rarely found in cross-fiber veins" because the "conditions prevailing at the time of their formation are not, as a rule, favorable for the solution and transportation of these minerals to a new place of deposition."

Although these veins may have resulted from lateral secretion during metamorphism, clear evidence of their replacement nature precludes the concept that they filled open fissures or forced their walls apart, as has been emphasized above. Furthermore, the irregular penetration of vein asbestos into the minerals along wall contacts suggests a process working outward by chemical attack from localized channels rather than one in which amphibole solutes migrated through the wallrock to concentrate in veins. There seems to be no obvious reason for postulating that the asbestos was introduced from a source outside the greenstones themselves, and the circumstances just mentioned argue that it was not derived by migration directly outward from the walls immediately adjacent. Therefore, we seem forced to the speculation that the vein-forming solutions were produced at somewhat lower levels in the greenstones (where, under greater temperature and pressure, they would achieve greater mobility and chemical potency) and migrated upward along certain permeable zones as replacing media. However, the discontinuous, lenticular character of thousands of seams of almost microscopic dimensions, which are not visibly interconnected or fed by larger ones, prevents ready acceptance of such an hypothesis and favors the alternative one of lateral secretion almost in situ. Yet these tiny veins offer the same objections to the latter as do their larger relatives. Consequently the source of the vein-forming material remains an open question.

*Cause of the Fibrous Structure.* Taber's explanation (1916A, p. 660) that fibers result from growth of crystals to which material is added *only at the base* by lateral secretion through closely-spaced openings in the wallrock could, obviously, only apply to the Virginia veins if the solutions migrated laterally directly from the walls opposite the ends of the fibers. Since there is some doubt concerning such migration, as pointed out above, his theory is also of questionable application on this point. Moreover, the writer has failed to find indications that the asbestos veins grew inward from opposite walls.

Peacock (1928, p. 279) points out that "the tendency for crystalline substances to develop normal to their bounding surfaces is too common and consistent to be insignificant." He conceives of a process in which the first thin layers of material deposited consist of crystals, oriented normal to the walls, which become elongated into cross-fiber veins as successive accretions are deposited in crystallographic continuity with them. Since, as Warren (1932) shows, actinolite has a ready tendency to develop an asbestiform habit because of its molecular structure, the mechanism suggested by Peacock seems more plausible and calls for less special conditions to produce cross-fiber veins of asbestos than does that of Taber. However, this mechanism as stated applies to the formation of amphibole veins by crystallization from a saturated solution in which the new material is added to the growing fibers on the ends which extend into the vein; whereas in replacement veins it is, presumably, added at the opposite ends, at the surfaces of contact with the material undergoing attack.

The writer ventures to suggest, therefore, a modification of Peacock's idea which might explain the fibrous structure of these Virginia deposits. He assumes (1) that the amphibole solutions migrated longitudinally along potential openings rather than laterally into them from the wallrock, and (2) that they permeated outward from such channels into the walls to form and widen veins by replacement. Then incipient crystals of the first thin film of actinolite to form were oriented normal to the bounding surfaces and had an inherent molecular tendency to develop fibers. Since the solutions were saturated, not with respect to these newly-deposited crystals, but, rather, with respect to the wallrock minerals, they did not precipitate directly upon the amphibole. Neither did they clog the grain boundaries or pores between the first layer of crystals with new material, but used them as avenues of penetration (and might even have diffused through the actinolite space-lattice) to reach the zone of attack on the opposite side of this first layer. Here, effecting an exchange of their substance for that of the feldspar, pyroxene, etc., they deposited another layer of actinolite whose crystalline masses obeyed the impulse to form in crystallographic continuity with those adjacent. Through continuous repetition of this process elongated fibers developed. Their length became varied somewhat because of differential permeability relations between them. Consequently, their contact with the wallrock very soon became highly irregular and remained so until the cessation of the process. Further study is required before this suggestion can be applied to the origin of those bodies of oblique-fiber and slip-fiber which are clearly not the result of post-vein deformation; but the suggested explanation seems reasonable for cross-fiber, and might need only minor qualifications to explain the others.

It should be noted, in passing, that no suggestion known to the writer regarding causes for fibrous structure is adequate to explain the fibers of non-uniformly oriented amphibole so abundant in these wallrocks. The conditions under which actinolite (and other minerals) sometimes appears fibrous, though commonly it is not, are but vaguely understood. Also it seems more than likely that the reason (or reasons) for uniformly-oriented fibers in fibrous veins constitutes a wholly separate problem.

*Possible Influence of Subjacent Intrusives on the Origin of the Fibrous Quartz.* The regional replacement of these asbestos seams by fibrous quartz must, likewise, involve a regional process. That the quartz was introduced from an external source after the metamorphism of these rocks is seen in the associated silicification and epidotization of the vein walls. Since such alteration partially obliterates foliated structures in the greenstones, the quartz must have been introduced later than the regional metamorphism.

Downward-moving meteoric waters operating near the surface could scarcely have had the chemical power to effect a widespread disappearance of amphibole and substitution of quartz. Moreover, nearly as many veins of almost pure asbestos, or of asbestos only partially replaced by quartz, are exposed as of fibrous quartz with residual actinolite. If near-surface waters were the agents, presumably they could operate at present and during the recent past as well as formerly, and almost no unreplaced veins should be found.

Hydrothermal solutions from magmatic sources would surely be capable of the transformation represented here, but would probably leave indications of their source in minerals of magmatic association within the veins or wallrocks. Since these have not been found, we must consider the alternate possibility that meteoric waters, heated and charged with chemical force in depth, or driven upward by approaching large, subjacent, intrusive masses of considerable areal extent, could attack the asbestos veins along certain zones determined by permeability relations.

The presence of such subjacent intrusive bodies younger than *part* of the Catoctin has been repeatedly indicated by several writers. Keith (1894) emphasizes the widespread injection of (his lower) Catoctin by granite; Weed and Watson (1906) reported "syenite" intruding greenstone farther south along the Blue Ridge; Miss Jonas (1927) stated that granite intrudes metabasalt in northern Virginia; the Geologic Map of Virginia 1928 lists the Catoctin as intruded by Hypersthene Granodiorite and Marshall Granite; Furcron (1934) emphatically insists that the Catoctin is intruded by granitic rocks, and shows (p. 404) dikes of granite in the greenstone; and the writer observed greenstone invaded by granite in northwestern Fauquier County.

Therefore, if we must appeal to magmatic sources for the heat and potency of the fibrous quartz solutions, they are clearly indicated in the literature. Further study is needed to settle the matter, but it is quite reasonable to consider that fibrous quartz in northern Virginia owes its presence to a sort of "sweating" in the greenstone roof over major plutonic injections.

## Summary

Brief consideration of the fibrous habit leads to the conclusion that some minerals are commonly asbestiform because of intramolecular forces peculiar to them, whereas others acquire it through special conditions of growth. Rarely fibrous minerals, usually associated with commonly-fibrous ones, derive their unusual features by concurrent growth, infiltration-molding, or replacement. All gradations are found between unit and aggregate pseudomorphs, the latter predominating among known occurrences; and residuals of the original mineral exist in all proportions within and between grains of the metacryst. Usage among geologists has extended Dana's definition of *fibrous* to include material which is fiber-like in gross outline only.

Published descriptions and the writer's studies of fibrous quartz indicate: that it is far more common than has been supposed; that it is not restricted to any type of rock, geologic horizon, mineral assemblage, or geographic location; that it is always of secondary origin. Recent discoveries of fibrous quartz in Virginia, Wyoming, and at five separate localities near Boston, Mass., are reported.

A widespread occurrence of fibrous quartz in cross-fiber actinolite seams (which were believed rare) is described in some detail, and the origin of both the asbestos and the quartz is considered. The wallrocks are chiefly extrusive metabasaltic, Pre-Cambrian volcanics, and the quartz-asbestos veins, more common in amygdaloidal facies, display most features typical of asbestiform veins. The fibrous quartz formed through aggregate replacement pseudomorphism of the asbestos in all stages. Earlier massive quartz, embedded in the fibrous quartz, lacks residual amphibole and is severely granulated. Although fibrous in major outlines, the later quartz is a granular mosaic in thin section. This paper shows that the asbestos exerted very little control on the character of its successor, that the fibrous quartz followed post-asbestos deformation and was accompanied by epidotization and silicification of the wallrocks, during which non-fibrous quartz permeated them as replacement veins.

That the asbestos veins formed by replacement, rather than by displacement of wallrocks through pressure developed by the growing fibers, is clear. The writer believes that the asbestos formed during regional metamorphism by lateral secretion. Objections are noted, however, both to the concept of a fiber-growth through additions from the walls directly opposite the fiber-ends and to that of an upward migration of amphibole solutes along vein channels.

A mechanism to explain the fibrous habit of the vein material is outlined, but conditions governing development of fibrous amphibole in the wallrocks are thought to constitute a wholly separate problem. The ababsence of fibrous quartz within the wallrocks is attributed to their lack of uniformly-oriented asbestos.

No minerals of magmatic origin, which would suggest that hydrothermal solutions direct from subjacent plutonic injections substituted fibrous quartz for amphibole, were observed. The writer emphasizes that several authorities agree on the invasion of part of the Catoctin greenstones by large granitic masses, and concludes that such bodies would have occasioned wholesale migration of heated meteoric waters as potential media of replacement through them to form the fibrous quartz.

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# PYROXMANGITE FROM INVERNESS-SHIRE, SCOTLAND

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The anorthic iron-manganese silicate, pyroxmangite has now been recognised from four localities: Iva (South Carolina); Tunaberg and Vester Silvberg, Sweden; Idaho.

At the Swedish localities the mineral was originally described under the name of sobralite (Palmgren 1917), but the comparative studies of Henderson and Glass (1936) have shown that sobralite has so close agreement in optical characters with the previously described pyroxmangite that the identity of these two minerals can be regarded as established.

The discovery of a further occurrence of pyroxmangite among the Lewisian rocks of Scotland has provided additional data on this interesting mineral.

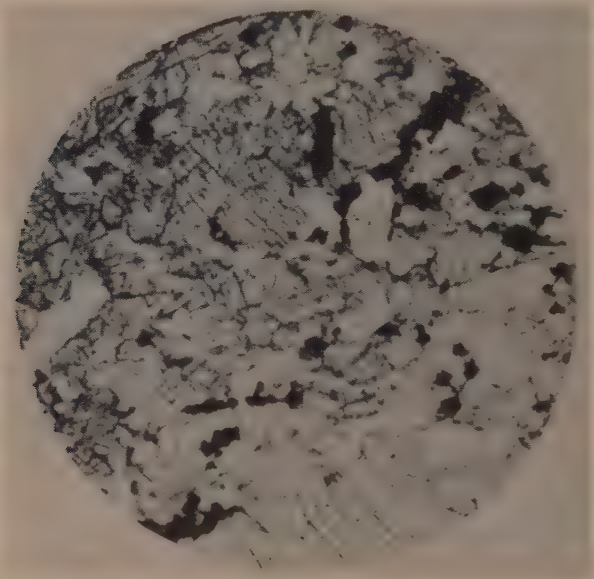

Fig. 1. Pyroxmangite-grunerite-garnet schist, Glen Beag, Glenelg, Inverness-shire. The constituents visible are pyroxmangite (most abundant), grunerite and magnetite. Spessartine-alamandine is present in adjacent portions of the slice. 26 diams.

The Lewisian inlier of Glenelg, Inverness-shire contains among its para-gneisses a group of manganiferous eulysites and related grunerite schists (Tilley 1936), and from one outcrop of these latter rocks both pyroxmangite and rhodonite are now recorded.

The pyroxmangite forms an important constituent of a manganiferous schist interbedded with a series of para-gneisses comprising biotite epidote gneisses, amphibole schists and lenses of limestone in the gorge of Glen Beag, Glenelg (1″ sheet 71, Geological Survey Scotland). The rock type with which the pyroxmangite is more intimately associated is a grunerite garnet schist carrying in places veins of rhodonite up to 1″ in width. The constituent minerals of the principal band of rock are grunerite, manganiferous garnet, magnetite, pyroxmangite together with accessory hedenbergite, iron hypersthene and pyrrhotite (Fig. 1).

Pyroxmangite in this rock occurs in pink grains of $\frac{1}{2}$–$\frac{3}{4}$ mm. average grain size. Exceptionally grains up to 5 mm. diameter may appear as porphyroblasts. In thin section the mineral is colourless and subidioblastic, usually tabular on (001) with a tendency to develop the forms of the two more prominent cleavages $m(110)$, $M(1\bar{1}0)$. A parting parallel to (010) is locally developed but a cleavage on (001) has been recognized only in crushed fragments under the microscope. A lamellar twinning on (010) is infrequently observed. As the extinction of the mineral is commonly somewhat undulose this twin development is probably of secondary origin. The birefringence of the mineral is distinctly greater than that of the rhodonites of the associated rocks. It is further distinguished by its much smaller optic axial angle. On material analysed $2V\gamma=41°$ while the rhodonites examined gave an average value $2V\gamma=74°$. Fragments resting on the principal cleavage (110) show an extinction $c\wedge\gamma'=32°$. In immersion liquids the refractive indices are determined as $\alpha 1.732$, $\beta 1.735$, $\gamma 1.750$. The mineral has a specific gravity of 3.63 and is unattacked by hydrochloric acid.

Pure material for analysis was selected from the crushed rocks by hand picking under a low power lens. This material gave the following result.

TABLE 1. ANALYSIS OF PYROXMANGITE FROM GLENELG
(Miss H. Bennett, analyst)

| | Analysis | Metal atoms on basis of 6 oxygen atoms | | |
|---|---|---|---|---|
| $SiO_2$ | 47.44 | 1.975 | 2.00 | |
| $Al_2O_3$ | 0.66 | 0.030 | | $\alpha 1.732$ |
| $Fe_2O_3$ | 1.45 | 0.045 | | $\beta 1.735$ |
| FeO | 15.02 | 0.522 | | $\gamma 1.750$ |
| MnO | 28.25 | 0.995 | 1.98 | $2V_\gamma 41°$ |
| MgO | 4.56 | 0.285 | | Sp. Gr. 3·63 |
| CaO | 3.00 | 0.135 | | |
| | 100.38 | | | |

TABLE 2. ANALYSES OF PYROXMANGITES AND IRON RHODONITE

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $SiO_2$ | 46.53 | 47.14 | 45.47 | 47.44 | 47.78 |
| $Al_2O_3$ | 0.21 | 2.38 | nil | 0.66 | 0.08 |
| $Fe_2O_3$ | 0.85 | — | 1.55 | 1.45 | 0.11 |
| FeO | 24.69 | 28.34 | 20.91 | 15.02 | 14.51 |
| MnO | 20.50 | 20.63 | 27.06 | 28.25 | 29.20 |
| MgO | 1.39 | — | 2.14 | 4.56 | 1.93 |
| CaO | 5.46 | 1.88 | 2.62 | 3.00 | 6.55 |
| $TiO_2$ | 0.08 | — | — | nil | — |
| | (BaO) | | | | |
| $H_2O$ | 0.39 | 0.33 | 0.32 | — | 0.09 |
| | 100.10 | 100.70 | 100.02 | 100.38 | 10.25 |

1. Sobralite, V. Silvberg, Sweden. (Sundius 1931.)
2. Pyroxmangite, Iva, South Carolina. (Ford and Bradley 1913.)
3. Pyroxmangite, Idaho. (Henderson and Glass 1936.)
4. Pyroxmangite, Glenelg, Scotland.
5. Rhodonite, Tuna Hästberg, Sweden. (Sundius 1931.)

The selected material contained no obvious mixed magnetite and in the interpretation of the analysis (Table 1) $Fe_2O_3$ has been treated as an integral constituent. The figures show good agreement with a metasilicate ratio.

When this analysis is compared with those of described pyroxmangites it is seen that the Glenelg mineral shows closest approximation in composition to the pyroxmangite of Idaho (Table 2, analysis 3). Its composition is, however, even closer to that of the iron rhodonite of Tuna Hästberg described by Sundius (Table 2, analysis 5); nevertheless the optical characters are more closely in agreement with those of pyroxmangites with varying iron and manganese contents (Table 3).

The contrasted optical properties of the Tuna Hästberg rhodonite and the Glenelg pyroxmangite afford support to the suggestion of Henderson and Glass (1936) that the two minerals are distinct species and are not members of a single continuously variable species. This suggestion had already been made by Sundius when he compared the optical characters of the Swedish sobralites with those of rhodonite.

Sundius (1931) has discussed the relations existing between the various manganese bearing compounds in the ternary system $MnSiO_3$–$FeSiO_3$–$CaSiO_3$. He concluded that the variation of optical characters in the group of bustamites were such that they could be regarded as manganese bearing wollastonites despite the fact that the most lime-rich bustamite contained only 52 wt. % of $CaSiO_3$.[1]

TABLE 3

| | % FeO | $\Delta$ | $2V$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|
| Pyroxmangite (Glenelg) | 15.02 | 0.018 | 41° | 1.732 | 1.735 | 1.750 |
| Rhodonite (Tuna Hästberg) | 14.51 | 0.012 | 70° | 1.725 | 1.728 | 1.737 |
| Pyroxmangite (Idaho) | 20.91 | 0.017 | 39° | 1.737 | 1.740 | 1.754 |
| Sobralite (V. Silvberg) | 24.69 | 0.017 | 42° | 1.738 | 1.740 | 1.755 |

Since the studies of Sundius our knowledge of the ternary system has been increased. Wollastonite since shown to be anorthic is now known to form an extended series of solid solutions in the system $CaSiO_3$–$FeSiO_3$ (Bowen and Schairer 1933). Bowen (1933) has further shown that crystals of the anorthic slag silicate vogtite (Hallimond 1919) can be reoriented and referred to a similar axial system as the anorthic wollastonite and has pointed out the isomorphous character of the two substances. The existence of a wide series of solid solutions including iron bearing wollastonites, bustamites and vogtite is thus to be envisaged. Among natural minerals the gap between wollastonite and the bustamites (analysis 25 of Fig. 2) is bridged only by the analysis of a manganwollastonite described by Goldschmidt (1911) from the Oslo field. The only optic data presented for this mineral is the value $2E=43°$ (cf. wollastonite $2E=69°$ $2V=40°$). Using a probable approximate value $\beta=1.640$, $2V$ for this mineral is 26°, significantly lower than the values for wollastonite or the most lime rich bustamite (analysis 25). These facts warrant a closer study of wollastonites of skarn deposits where manganiferous wollastonites with still lower optic axial angles may occur.

The compositions of the anorthic minerals of the system $MnSiO_3$–$FeSiO_3$–$CaSiO_3$ are indicated in the ternary plot of Fig. 2, the key to which is indicated in the description subjoined to Fig. 2. The content in MgO of the natural minerals, usually small in amount is calculated as $MgSiO_3$ and added to $CaSiO_3$. If optical data were not under consideration it would have been more appropriate to consider $MgSiO_3$ with $FeSiO_3$.

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[1] The lattice dimensions of bustamite have since been shown to have values close to those of wollastonite (Berman and Gonyer 1936).

Sundius inferred that bustamite and rhodonite were distinct minerals. This opinion was based on a discontinuity revealed in the optical properties of analysed iron poor rhodonites and bustamites and furthermore by the occurrence together in intimate association of these two minerals in rocks as at Långban.

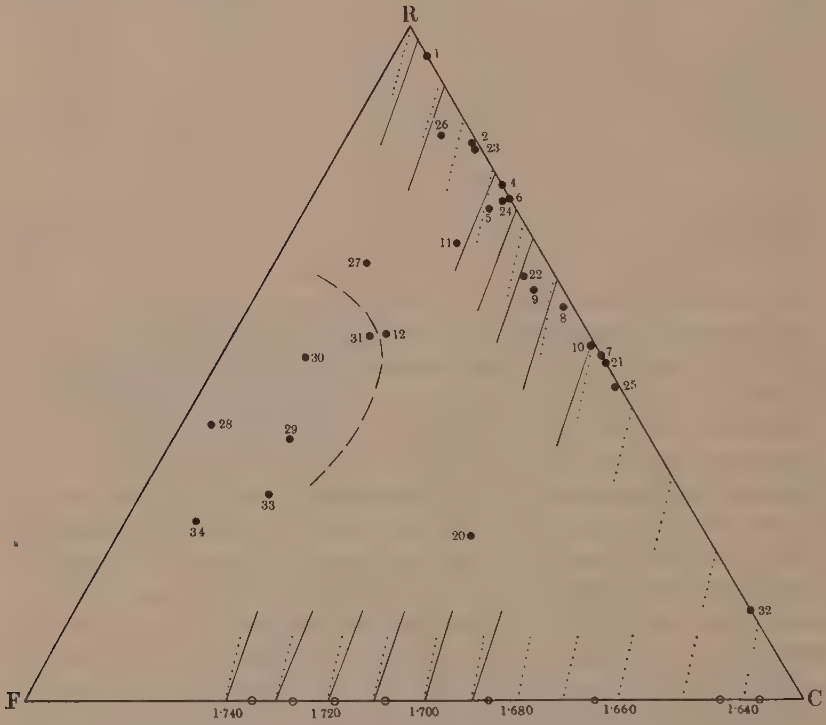

FIG. 2. Compositions of rhodonites, bustamites and pyroxmangites in the system $MnSiO_3$ (R), $FeSiO_3$ (F), $(CaMg)SiO_3$ (C) (wt. %).

The numbers refer to analyses of minerals as follows: 1–12 (Sundius 1931), Table I, p. 517); 20 (Hallimond 1919); 21–23 (Hey 1929); 24–25 (Larsen and Shannon 1922); 26–30 (Henderson and Glass 1936); 31 Glenelg pyroxmangite; 32 (Goldschmidt 1911); 33, 34 (Whiteley and Hallimond 1919). Open circles—wollastonite solid solutions (Bowen-Schairer 1933).

Further data on the system $CaSiO_3$–$MnSiO_3$ are provided by the experimental studies of Voos (1935). He has presented his results in the form of a binary diagram showing complete miscibility between wollastonite ($\beta$ $CaSiO_3$) and the compound $MnSiO_3$. The optical data of this continuous solid solution series is given in graphical form and shows divergence from the values for the natural rhodonites and bustamites studied by Sundius.

From a study of *x*-ray powder photographs of his synthetic preparations Voos confirms the deduction from his thermal data but also states that the rhodonite (analysis 1) and bustamite (analysis 7) of Sundius show complete identity with the synthetic products of corresponding composition. Nevertheless the optic data are not in accord. The synthetic products show a value of the $\gamma$ index on an average 0.01 lower than the natural products. This discrepancy holds for minerals which contain insignificant contents of MgO and FeO.

This is made evident in Fig. 2 where the interpolated $\gamma$ values of the iron wollastonite solid solution series is projected (a) towards the interpolated $\gamma$ values of rhodonites and bustamites (full lines), (b) towards the interpolated $\gamma$ values of the synthetic $CaSiO_3$–$MnSiO_3$ solid solutions (dotted lines).

The manner in which the optic data on the synthetic $CaSiO_3$–$MnSiO_3$ solid solutions has been obtained lead us to except no great accuracy in the results. The synthetic products are reported as developing in fibrous aggregates and apparently only approximate maximum and minimum refractions ($\gamma'$, $\alpha'$) were obtained. Until data in this system on homogeneous single crystals are provided the values of Voos should be treated with reserve. At the same time it must be remembered that Sundius by expressing his data on a binary diagram is treating (Fe, Mn) and (Ca, Mg) each as single variables. His curves are drawn on minerals showing up to 3.8 molecular per cent $FeSiO_3$ (analysis 5) and 14.20 per cent $MgSiO_3$ (analysis 6) and it is still questionable whether notable discontinuities would be revealed in a true binary system (Ca, Mn). The existence side by side in rocks of bustamite and rhodonite may simply be an expression of limited miscibility at low temperatures.

In the interior of the plot the paucity of data prohibits any conclusion as to the detailed course of the $\gamma$ isofracts within the ternary system. The optical data on vogtite show $\beta$ 1.701 but this compound contains more than 13 wt. per cent of $MgSiO_3$.

In the diagram the field of the analyses of pyroxmangites has been separated on the basis of the distinctive properties of this group of minerals compared to the rhodonites.

Two other analyses—those of "iron rhodonites" from slags described by Whiteley and Hallimond (1919) may be referred to here. They have the following compositions (analyses 33, 34, Fig. 2):

| | $MnSiO_3$ | $FeSiO_3$ | $MgSiO_3$ | $CaSiO_3$ |
|---|---|---|---|---|
| 33 | 30.5 | 53 | 5 | 11.5 |
| 34 | 26.8 | 64.2 | n.d. | n.d. |

The compositions of both these "iron rhodonites" lie on the $FeSiO_3$ side of the field of the analysed pyroxmangites. No optic data of these compounds has hitherto been published and I am indebted to Dr A. F. Hallimond for a specimen of No. 34 on which the following data have been determined. The crystals show the characteristic rhodonite cleavages parallel to $m(110)$ and $M(1\bar{1}0)$ and fragments mounted in immersion liquids show a characteristic extinction angle of 30°–32° ($c \wedge \gamma'$) when lying on the best cleavage (110). The optic data presented below show a remarkable agreement with those of pyroxmangites and are compared here with the most iron rich pyroxmangite of Iva, South Carolina.

| Pyroxmangite Iva, South Carolina | | "Iron Rhodonite" (34), acid slag | |
|---|---|---|---|
| $FeSiO_3$ | 55 | $FeSiO_3$ | 64.2 |
| $MnSiO_3$ | 41 | $MnSiO_3$ | 26.8 |
| $CaSiO_3$ | 4 | $(CaMg)SiO_3$ | n.d. |
| $\alpha 1.748$ | | $\alpha 1.750$ | |
| $\beta 1.750$ | | $\beta 1.754$ | |
| $\gamma 1.746$ | | $\gamma 1.767$ | |
| $2V\gamma 37°$ | | $2V\gamma 27°$ | |

In Fig. 3 are plotted the approximate compositions of the three slags (indicated by arrow heads) described by Whiteley and Hallimond as well as the compositions of the three metasilicates (20, 33, 34) (indicated by circles) contained in the respective slags. The duplication indicated refers to alternative methods of grouping MgO with FeO (full lines) or with CaO (dotted lines). In the case of slag 33 the crystallisation of

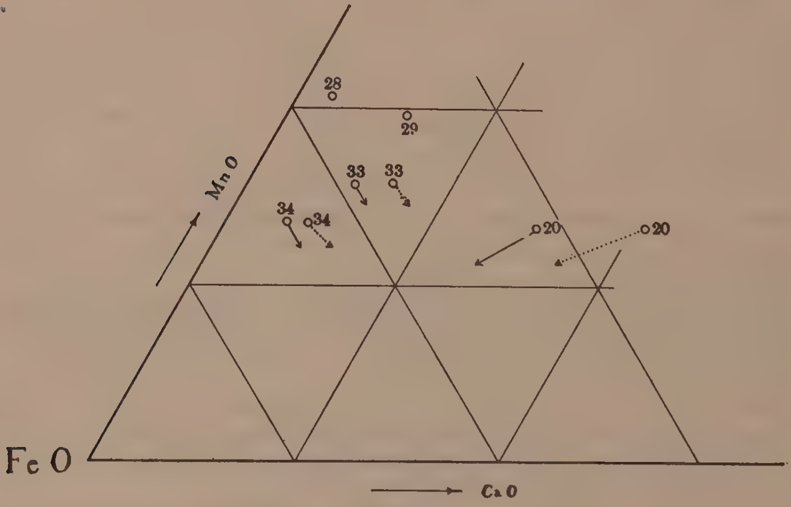

FIG. 3

metasilicate was preceded by that of cristobalite but metasilicate formed the primary phase in slags 20 and 34.

The pyroxmangites and the slag compound (34) show greater distinctions in optical properties from vogtite than this compound does from the iron-bearing wollastonite, e.g.

| | $FeSiO_3$ | 2V | sign | $\gamma$ |
|---|---|---|---|---|
| Slag crystals (34) | 64.2 | 37° | positive | 1.767 |
| Vogtite (20) | | 65.5° | negative | 1.701($\beta$) |
| Iron wollastonite | 70.0 | 85° | negative | 1.734 |

but there is a considerable gap to be bridged between the compositions of these three solid solutions. On the other hand the pyroxmangites show a considerable range of composition with but moderate variation in optical characters. Hallimond and Whiteley indeed were of opinion that their "iron rhodonites" and vogtite were distinct, vogtite crystallising from the slags with more than 8 per cent CaO and giving these slags an acicular fracture. Further support for this opinion is given by Dr. Hallimond who has informed me that slags were obtained in which vogtite and "iron rhodonite" occurred together as distinct phases. The optic data now presented are in harmony with this view and point furthermore to the probable identity of this slag mineral with pyroxmangite which is itself distinct from rhodonite. A comparative *x*-ray study of these solid solutions is now in progress at Cambridge.

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# THE SPACE-GROUP AND UNIT CELL OF SYLVANITE

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Faceted crystals of sylvanite from Cripple Creek, Colorado (kindly furnished by Prof. Charles Palache of Harvard University) and from Săcărâmbu (Nagy-Ág), Transilvania (kindly supplied by Dr. W. F. Foshag of the U. S. National Museum) were investigated by means of the Weissenberg *x*-ray goniometer. Rotation photographs were made around the principal zone-axis, also Weissenberg photographs of the equator and first and second layer-lines. Copper K- and chromium K-radiation was used. The Weissenberg photographs were analyzed graphically by the method of Schneider (1928). New crystallographic axes were chosen to conform with the arrangement of the symmetry elements assumed in the International Tables for the Determination of Crystal Structures. The dimensions of the structural unit cell, all determined by purely röntgenographic measurements, are $a_0 = 8.94$ Å, $b_0 = 4.48$ Å, $c_0 = 14.59$ Å, all $\pm 0.02$ Å; $\beta = 145° \ 26' \pm 20'$. Diffraction effects were obtained from the following planes: *u*00, *g*00, 0*u*0, 0*g*0, 00*g*, 0*uu*, 0*ug*, 0*gu*, 0*gg*, *u*0*g*, *g*0*g*, *ug*0, *gu*0, *gg*0, *uuu*, *uug*, *ugu*, *ugg*, *guu*, *gug*, *ggu*, *ggg* where *u* denotes any odd number and *g* denotes any even number. No diffraction effects were obtained from the following: 00*u*, *u*0*u*, *g*0*u*, *uu*0. Thus sylvanite belongs either to the space-group $Pc - C_s^2$ or to the space-group $P2/c - C_{2h}^4$, both of which are characterized by the absence of diffraction effects from 00*u*, *u*0*u*, and *g*0*u*, due to the presence of a glide-plane parallel to 010 with a glide component $c/2$. Absence of diffraction effects from *uu*0 is not a characteristic of any monoclinic space-group and is a consequence of the special set of parameter values in the sylvanite structure. Faceted crystals of sylvanite have been studied with the reflection goniometer by several investigators. Projections of such crystals drawn by Koksharov, Schrauf, Vrba, and Palache and reproduced by Goldschmidt (1923) show the habit of sylvanite to be holohedral. Consequently the space-group of sylvanite appears to be $P2/c - C_{2h}^4$. The chemical analysis of crystallographically studied material made by Palache (1900) corresponds to the composition $(Au, Ag)Te_2$ with a ratio of gold to silver equal to 1.15. The density determined by Palache (1900) on three isolated crystals by means of the hydrostatic balance is 8.16. The density computed from the *x*-ray measurements on the assumption that the formula is $AuAgTe_4$ is 8.11; if the gold-silver ratio is taken as 1.15 instead of 1.00 and if, as appears probable, the slight excess of gold is the result of replacement of silver atoms by gold atoms in the structure, the corresponding *x*-ray density would be 8.17. The agreement of the measured and calculated densities leaves no doubt that the number of "molecules" of $AuAgTe_4$ in the unit cell is two.

Sylvanite was first proved to belong to the monoclinic system by Koksharov (1866, 1888), who calculated the following axial elements from measurements made on one twinned crystal and determined the twin-plane:

$$a_K:b_K:c_K = 1.7732:1:08890,\ \gamma_K = 55°21\tfrac{1}{2}';$$

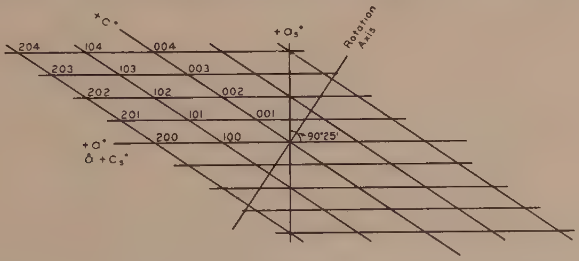
here $a_K$ denotes the vertical axis, $b_K$ the clinodiagonal axis, $c_K$ the orthodiagonal axis, and $\gamma_K$ the angle which the clinodiagonal axis makes with the vertical axis. The directions of Koksharov's axes are those of possible structural axes, but to obtain the structural lattice the unit length of his *b*-axis (i.e. his clinodiagonal axis) must be multiplied by two. The corresponding values of the axial elements in terms of the present writers' axes are given in Table 1 for comparison with the values obtained by *x*-ray analysis.

TABLE 1. AXIAL ELEMENTS OF SYLVANITE

A comparison of the transformed axial elements of Koksharov and of Schrauf with those of Tunell and Ksanda

| | | $a\ :b:\ c$ | $\beta$ |
|---|---|---|---|
| Koksharov | (reflection goniometer) | 1.9947:1:3.2822; | 145°40′ |
| Schrauf | (reflection goniometer) | 1.9914:1:3.2679; | 145 33 |
| Tunell and Ksanda | (*x*-ray goniometer) | 1.9955:1:3.2567; | 145 26 |

An elaborate study of the morphology of sylvanite was made by Schrauf (1878) on numerous crystals from Transilvania (Siebenbürgen). The relationship between the axes chosen by the present writers for purposes of structural analysis and those of Schrauf is indicated in Fig. 1, which is a section of the reciprocal lattice through the origin parallel to the symmetry plane. The reciprocal axes of Tunell and Ksanda are let-



Sylvanite

Section of reciprocal lattice through origin parallel to symmetry plane

FIG. 1

tered $a^*$ and $c^*$; reciprocal axes corresponding to the linear axes of Schrauf are lettered $a_S^*$ and $c_S^*$. The linear axial elements of Schrauf do not correspond to the relative dimensions of a possible unit cell in the structure and for this reason were not retained for purposes of structural analysis. The axial elements calculated by Schrauf are:

$$a_S:b_S:c_S = 1.6339:1:1.1265;\ \beta_S = 90°25'.$$

The corresponding values of the axial elements in terms of the present writers' axes are given in Table 1 for comparison with the values obtained by $x$-ray analysis.

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# CRYSTALLOGRAPHY OF HERAPATHITE

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After a century of obscurity, the artificial crystal, herapathite, has lately assumed, by virtue of its extraordinary dichroism, a technical importance hardly second to that of more familiar natural crystalline materials such as quartz and calcite. This situation has arisen through the recent successful preparation of large area transmission polarisers (Polaroid, Herotar, etc.) using herapathite as starting material, by several different processes on both sides of the Atlantic. Under such circumstances the geometrical and optical properties of herapathite deserve more study than they have hitherto received in the literature of crystallography. It is hoped that the present account, while far from definitive, will at least begin to fill this deficiency.

*Composition.* The composition of herapathite has been shown by Jörgensen (1877) and others to be (I) $4\mathbf{C}H_2\cdot 3SO_4\cdot 2I_3\cdot 6H_2O$, where **C** denotes the quinine molecule $C_{20}H_{24}N_2O_2$. The crystal can give up at least some of its water without losing its form and optical properties. It is an acid sulfate triiodide of quinine. Jörgensen found several other crystals built up of the components **C**, $H_2SO_4$, HI, $I_2$, having crystal forms and optical properties closely similar to those of herapathite. His formulas for three of these herapathitic crystals may be written, for convenience, $4\mathbf{C}H_2\cdot 3SO_4\cdot 2I\cdot I_n$, where $n=5, 6, 7$ (compounds II, III, IV), and for a fourth crystal (VI) $4\mathbf{C}H_2\cdot 2SO_4\cdot 4I_3$. Jörgensen also found several selenate herapathites having crystal forms and compositions corresponding to the foregoing sulfate herapathites, notably (I) and (III).

Although the crystals examined in the course of the present work were not analysed, there can be no doubt that they belong to Jörgensen's isostructural group and are fairly representative. They are fragile brown plates up to 1 cm. in diameter found in several different herapathite preparations; the latter had been precipitated in a finely divided form about two years previously and left standing under the mother liquor in sealed containers, where they had obviously recrystallised. In addition some smaller green plates, the familiar form of herapathite described in the literature, were also examined.

*Morphology.* The crystal plates belong to the orthorhombic system, the somewhat irregular development of the pyramid faces leaves the symmetry class in doubt. The $a$-axis is taken as the plate normal, the $c$-axis as the direction in the plate parallel to which light vibrations are strongly absorbed; the plates are sometimes elongated along $b$. Light vibrations parallel to the $a$ and $b$ axes are freely transmitted.

Lot 1 (brown crystals). The density measured by suspension is 1.645. The axial ratio, averaged from two-circle measurements of four selected crystals measured with reference to the *b*-axis, is $a:b:c=2.202:1:1.268$. The crystals show the forms {100} (plate face), {110}, {310}, {101}, {201} and {211}. Another preparation shows the form {321} also. Measurements of Lot 1 are summarized in Table 1, and a drawing is shown in Fig. 1.

TABLE 1. HERAPATHITE (LOT 1). TWO-CIRCLE ANGLES

$a:b:c=2.2020:1:1.2679;\ r_2:p_2:q_2=0.7887:0.4541:1$

| Form | Faces | Measured Limits | | Measured Mean | | Calculated | |
|---|---|---|---|---|---|---|---|
| | | $\phi_2$ | $\rho_2$ | $\phi_2$ | $\rho_2$ | $\phi_2$ | $\rho_2$ |
| 100 | 8 | — | — | 0°00′ | 90°00′ | 0°00′ | 90°00′ |
| 110 | 6 | — | 24°19′–24°37′ | 0 00 | 24 28 | 0 00 | 24 25½ |
| 310 | 2 | — | 53 12 –53 18 | 0 00 | 53 15 | 0 00 | 53 43 |
| 101 | 12 | 59°16′–60°18′ | — | 60 02 | 90 00 | 60 04 | 90 00 |
| 201 | 4 | 40 10 –41 31 | — | 40 49 | 90 00 | 40 58 | 90 00 |
| 211 | 8 | 40 40 –41 42½ | 49 49 –50 37 | 41 06½ | 50 24 | 40 58 | 50 16 |
| (321 | 2 | 29 40 –32 02 | — | 30 51 | 38 55 | 30 04 | 38 12½) |

Lot 2 (brown crystals). Three crystals measured in normal position yield the axial ratio 2.251:1:1.268. Forms observed are {100}, {110}, {210}, {101}, {211}; the measurements are summarised in Table 2.

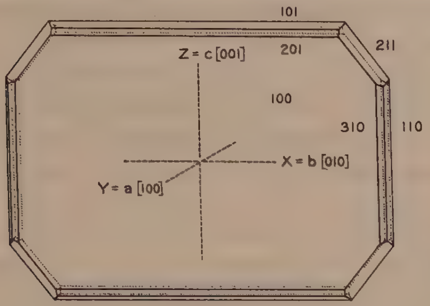
TABLE 2. HERAPATHITE (LOT 2): TWO-CIRCLE ANGLES

$a:b:c=2.2515:1:1.2679;\ p_0:q_0:r_0=0.5631:1.2679:1$

| Form | Faces | Measured Limits | | Measured Mean | | Calculated | |
|---|---|---|---|---|---|---|---|
| | | $\phi$ | $\rho$ | $\phi$ | $\rho$ | $\phi$ | $\rho$ |
| 100 | 6 | — | — | 90 00′ | 90 00′ | 90°00′ | 90°00′ |
| 110 | 9 | 22°50′–24°10′ | — | 23 35 | 90 00 | 23 57 | 90 00 |
| 310 | 9 | 52 49 –53 46 | — | 53 21 | 90 00 | 53 07 | 90 00 |
| 101 | 5 | — | 29°15′–29°33′ | 90 00 | 29 23 | 90 00 | 29 23 |
| 211 | 7 | 41 20 –42 39 | 59 08 –59 47 | 41 52 | 59 21 | 41 37 | 59 28½ |

Lot 3 (small green crystals). On one plate it was possible to make approximate settings on the extremely narrow edges of {110} (4 faces) and {101} (2 faces). These give the average values $\phi(110)=23°53'$, $\rho(101)=29°19'$, which by chance agree well with values found for Lot 2 (table 2).

Lot 4 (small green crystals). The density by suspension is 1.700; this figure is somewhat higher than that given for Lot 1, and very much lower than 1.895 as given by Herapath (1855). The corners of the rectangular plates are cut off by two oblique edges (Fig. 2). For comparison with the measurements of Herapath, and of Jörgensen, I measured the angles $A_1$ and $A_2$ with a petrographic microscope. If the edges are taken to represent intersections of faces ($h$11) and ($h$12) with (100), satisfactory agreement is found not only with the earlier work, but also with the present goniometric measurements.



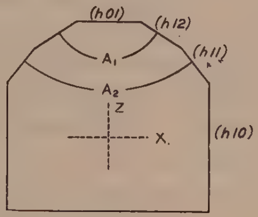


FIG. 1 (left). Herapathite, faces and optical orientation.
FIG. 2 (right). Herapathite, edge angles and optical orientation.

| | H. | J. | W. | calc. |
|---|---|---|---|---|
| $A_1$ ($h$12) | 115° | 116° | 116.4° | 115.3° |
| $A_2$ ($h$11) | 75 | 77 | 77.5 | 76.5 |

The calculated values of these two angles are here based on $b:c=1:1.268$.

It will be noted that while ($h$11) may be the same as (211) given above, no face corresponding to ($h$12) was found with the goniometer.

With reference to the optical orientation, the direction designated as the "plane of polarisation" of the incident light by Herapath and Jörgensen must be taken as perpendicular to the direction now conventionally denoted by the "vibration direction" of the light. The orientation stated by Groth (1907) is incorrect.

*Optics.* A complete optical investigation of the herapathite crystal would define its absorption, its reflection and its refraction for a light ray, polarised in any azimuth, propagated in any direction relative to the crystallographic axes, and incident on any section of the crystal. Obviously this would be a formidable task.

As previously stated, the absorption for light vibrating parallel to $c$ is enormously greater than that for light vibrating parallel to $a$ or $b$; indeed, in the basal section the latter two axes cannot be distinguished in their absorption. The absorption ellipsoid is thus in effect a rotation surface greatly elongated along its axis which coincides with the *c*-axis of the crystal. Data on the double absorption of herapathite, in relative measure, for the visible spectrum have recently been published by Haase (1936).

The reflection and absorption of herapathite crystals were described in an early paper by Haidinger (1853).

I measured the principal refractive indices by the immersion method in Na light as: $\alpha \| b = 1.608$, $\beta \| a = 1.625$. It will be possible to measure $\gamma$ directly by transmission only with far red or infra red light. Thin basal sections in convergent light show a typical positive acute bisectrix figure, at least for rays of not too great obliquity. The optic axes lie in the (100) plane, the angle between them is small with 2V estimated at about 10°, the dispersion is moderate with red $>$ green. Blue green light of $\lambda$ about 490 $m\mu$ is already quite strongly absorbed, while 530 $m\mu$ is readily transmitted.

*X-ray Measurements.* The absolute axial lengths of crystals of Lot 1 were measured approximately from layer line separations of rotation photographs (CuK) as follows: $a_0 : b_0 : c_0 = 33.30 : 15.15 : 19.24$ AU$= 2.198 : 1 : 1.270$, in agreement with the goniometric values.

From these axes the molecular weight is calculated as follows:

$V = abc = 9720$ AU$^3$
$M = DV/Z = 2428$, based on $D = 1.645$, $Z = 4$
$M = 2355$ for (I) $4C_{20}H_{24}N_2O_2 \cdot 3H_2SO_4 \cdot 2HI_3$
or 2463 for the same formula plus $6H_2O$.

The unit cell of herapathite is an unusually large one. In accord with the orthorhombic symmetry the contents are to be distributed over 2, 4, 8 and 16-fold points; for example

(I) $16CH_2 \cdot 8SO_4 \cdot 4SO_4 8I_3$.

Jörgensen's isostructural crystals might than have some such distributions as:

(II) $16CH_2 \cdot 8SO_4 \cdot 4SO_4 \cdot 6I_3 + 2I_5$,
(III) $16CH_2 \cdot 8SO_4 \cdot 4I_3 + 4I_5$,
(IV) $16CH_2 \cdot 8SO_4 \cdot 4SO_4 \cdot 4I_3 + 2I_5 + 2I_7$.

The last crystal has an excess of four structural units (triiodide ions) over the first four, thus:

(VI) $16CH_2 \cdot 8SO_4 \cdot 4I_3 \cdot 8I_3 + 4I_3$.

Alternative distributions can be easily formulated, the ones given are purely for the sake of illustration. They serve to show that the cell volume found above is large enough so that all the iodine atoms in the several crystals, assuming that they all have the same unit cell, can be present in the form of polyiodide ions of the general formula $(I_{2n+1})^-$.

The unusual optical properties of this isostructural group of crystals and of other strongly dichroic crystals containing iodine may be supposed to be due, first to a linear configuration of the polyiodide ions $(I_{2n+1})^-$, second to the orientation of the axes of all these polyiodide ions parallel to the *c*-axis of the crystal. It should prove possible to test this supposition by an analysis of *x*-ray diffraction data.

*Acknowledgment.* The writer is indebted to Mr. E. H. Land for the material on which the foregoing measurements are based, to Professor Charles Palache for the opportunity to carry out the work in the laboratories of Harvard University during the winter 1935–1936.

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# RE-ORIENTATION OF RÖMERITE

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Römerite—$Fe_2'''Fe''(SO_4)_4 \cdot 14H_2O$, from near Goslar in the Harz, was named by Grailich (1858). The first adequate crystallographic work on the species was that of Blaas (1884) who studied crystals from Persia and obtained triclinic elements which were adopted with minor corrections by Goldschmidt in the *Index* (1891). Linck (1888) measured crystals of römerite from Chile and computed triclinic elements in a new setting; these are given in corrected form by Dana (1892). Scharizer (1913) took still another position, computing new elements from Linck's measurements; these are reproduced, with a considerable change in the $a$-axis, by Doelter (1927). Finally, Ungemach (1935) adopted Linck's setting in preference to that of Blaas, and calculated new elements considerably different from those of Linck, from careful measurements on crystals with many new forms from Tierra Amarilla in Chile. Römerite thus presents a situation which is common among triclinic species, namely a multiplicity of published crystallographic orientations representing only a few of the scores of settings which will satisfy the usual loosely defined requirements of an acceptable triclinic orientation.

In preparing a definitive crystallographic presentation the choice of setting requires first consideration. If there is a unique setting that expresses generally accepted morphological and structural requirements and can easily be reached by different workers, such a setting has great advantages over an arbitrary orientation. The normal triclinic setting of Peacock (1937) meets these requirements. It is defined as the unique setting in which the geometrical elements correspond to the cell given by the three shortest non-coplanar identity periods in the structural lattice, in the one orientation in which the axis of the main zone is $c[001]$, the axial angles $\alpha$ and $\beta$ are both obtuse, and the axis $b[010]$ is longer than the axis $a[100]$. From this definition it follows that the axial planes are the three planes with the greatest spacings in the structural lattice; consequently, the reciprocal axial periods are also the three shortest periods in the reciprocal structural lattice. The condition that $\alpha$ and $\beta$ are both obtuse results from the conventional attitude of the base, which slopes to the front-right ($\phi_{001}=0°–90°$); while the condition that $b[010]$ is greater than $a[100]$ causes the projected reciprocal lattice period $p_0'$ to be greater than the projected period $q_0'$. A common, but not infallible, consequence of the normal setting is that [001] is the shortest direct lattice period, while (010) is the plane with the greatest spacing and therefore the most probable cleavage.

Peacock (1937) and Richmond (1937) have shown how the normal setting can be found from the external geometry of triclinic crystals, the correctness in both cases being proved by subsequent, independent determinations of the structural lattices. In the present case a confirmatory röntgenographic determination is unnecessary, since the gnomonic projection of the forms on the plane normal to the axis of the main zone presents the perfectly ideal aspect of the normal setting. In the papers mentioned the method of recomputing triclinic elements to a new setting is not explained; and since this process is not concisely given in the accessible texts an outline of the method may be useful.

The forms of römerite in Linck's position, according to Ungemach (1935, p. 161), are shown in stereographic projection in figure 1. One observes the weakness of the vertical zone [001], which has only three forms; the steepness of the parametral plane (111), yielding a relatively long vertical axis; and the marked eccentricity of the pole of the base (001), indicating axes of considerable obliquity. These features are all at variance with the principles of the normal setting.

Linck's zone [(001)(010]=[100], with twelve forms, is clearly the main zone; this is supported by Ungemach's words: "La zone $p$ $g^1$ est toujours richement développée." Allowing for the viewpoint adopted in Ungemach's figures 18 and 19, the axis [100] also appears to be the axis of morphological elongation. Swinging the poles in our figure 1 forward about the normal to (010) until (001) falls into the primitive circle, projecting each stereographic point into its gnomonic position, and turning the combined stereographic-gnomonic projection about the vertical axis into the one position in which the requirements of the normal setting are satisfied, we obtain the relations in figure 2. In this figure the small points are the stereographic points in the new position; the larger filled points are the gnomonic points of the terminal planes; the radial lines drawn from (001) to ($hk1$) are normals to the vertical planes ($hk0$).

Since the gnomonic terminal points fall without exception at the nodes of a plane lattice, this lattice is unquestionably the first layer of the reciprocal structural lattice. The three shortest periods in this reciprocal lattice are: $p_0'=(001)-(101)=(000)-(100)$; $q_0'=(001)-(011)=(000)-(010)$; $r_0'=(000)-(001)$. The lengths $p_0'$, $q_0'$, are measured directly on the gnomonic projection; $r_0'$, the distance from (001) to the center of the sphere of projection, is obtained by a simple construction. The reciprocal axial angles $\lambda=(010):(001)$, $\mu=(001):(100)$, $\nu=(100):(010)$, are most easily measured in the stereographic projection. Thus we obtain graphical values for the elements of the new reciprocal lattice which are useful in checking subsequent calculations.

In the normal setting Linck's axial planes and parametral plane receive new symbols, as follows:

Linck Wolfe
$(100)=(00\bar{1})$
$(010)=(1\bar{1}0)$
$(001)=(0\bar{1}0)$
$(111)=(1\bar{2}\bar{1})$

This equivalence gives the transformation formula, Linck to Wolfe: $010/0\bar{1}\bar{1}/\bar{1}00$, whereby all Ungemach's face symbols are rapidly transformed to the new setting.

The transformation formula has another property which is invaluable in the present connection; it gives directly the symbols $[uvw]$ of the new axes in the old lattice, which we require for computing the new lattice elements, $a', b', c'; \alpha', \beta', \gamma'$, from the old lattice elements, $a, b, c; \alpha, \beta, \gamma$. We can write at once:

| Wolfe | Linck | |
|---|---|---|
| $a'[100]$ | $=[010]$ | $= b$ |
| $b'[010]$ | $=[0\bar{1}\bar{1}]$ | $=$ — |
| $c'[001]$ | $=[\bar{1}00]$ | $= -a$ |
| $\alpha'=[010]:[001]$ | $=[0\bar{1}\bar{1}]:[\bar{1}00]$ | $=$ — |
| $\beta'=[001]:[100]$ | $=[\bar{1}00]:[010]$ | $= 180^0\text{-}\gamma$ |
| $\gamma'=[100]:[010]$ | $=[010]:[0\bar{1}\bar{1}]$ | $=$ — |

Only three of the new elements, namely $b'$, $\alpha'$, $\gamma'$, require to be computed. The length $b'$ we obtain from the general formula: $T^2_{uvw}=a^2u^2+b^2v^2+c^2w^2+2bcvw\cos\alpha+2cawu\cos\beta+2abuv\cos\gamma$, where $T_{uvw}$ is the translation distance (identity period) in the old lattice row $[uvw]$. The angles $\alpha'$, $\gamma'$, are obtained by the general expression: $\cos\tau=[a^2u_1u_2+b^2v_1v_2+c^2w_1w_2+bc(v_1w_2+w_1v_2)\cos\alpha+ca(w_1u_2+u_1w_2)\cos\beta+ab(u_1v_2+v_1u_2)\cos\gamma]/T_{u_1v_1w_1}\cdot T_{u_2v_2w_2}$, in which $\tau$ is the angle between the rows $[u_1v_1w_1]$ and $[u_2v_2w_2]$ in the old lattice. In this case, as in most special cases, many terms vanish in the general equations. In computing lattice angles it is necessary to write the symbols of the lattice rows in proper cyclic order to ensure that the value of the cosine of the angle sought has the proper sign.

The correctness of the foregoing calculations can be verified by calculating the volumes of the elementary cells from both sets of elements from the formula:

$$V = abc\sqrt{(1+2\cos\alpha\cos\beta\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma)}.$$

The volumes are bound to be integrally related; in the present case they are identical, since both cells are unit cells of the same lattice; the value obtained from both sets of elements is $V=2.3035$.

Thus from Ungemach's elements for römerite in Linck's setting:

$a:b:c=0.99035:1:2.6460;\qquad \alpha=116°37', \beta=95°06', \gamma=79°30'$

we obtain the normal elements:

$$a':b':c' = 0.4214:1:0.4174; \qquad \alpha' = 91°17', \beta' = 100°30', \gamma' = 85°31'$$

In conclusion we give a presentation of the morphological crystallography of römerite which follows the form used by Palache in Peacock (1937). The addition of Dana's form letters, which are often used alone in describing crystal forms, permits ready correlation of the old and new notations.

RÖMERITE[1]—$Fe_2'''Fe''(SO_4)_4 \cdot 14H_2O$

Triclinic; pinacoidal—$\bar{1}$

$a:b:c = 0.4214:1:0.4174$; $\alpha = 91°17'$, $\beta = 100°30'$, $\gamma = 85°31'$[2]
$p_0:q_0:r_0 = 0.9931:0.4116:1$; $\lambda = 89°31\frac{1}{2}'$, $\mu = 79°34'$, $\nu = 94°19\frac{1}{2}'$
$p_0' = 1.0101$, $q_0' = 0.4186$; $x_0' = 0.1853$, $y_0' = 0.0084$

| Forms[3] | $\phi$ | $\rho$ | *A* | *B* | *C* | Dana |
|---|---|---|---|---|---|---|
| *c* 001 | 87°24½′ | 10°30′ | 79°34′ | 89°31½′ | 0°00′ | *a* |
| *b* 010 | 0 00 | 90 00 | 94 19½ | 0 00 | 89 31½ | *c* |
| *a* 100 | 94 19½ | 90 00 | 0 00 | 94 19½ | 79 34 | *q* |
| *i* 140 | 32 13 | 90 00 | 62 06½ | 32 13 | 84 01½ | — |
| *j* 130 | 40 29 | 90 00 | 53 50 | 40 29 | 82 51 | *l* |
| *k* 120 | 52 55 | 90 00 | 41 24 | 52 55 | 81 21½ | *s* |
| *m* 110 | 71 13 | 90 00 | 23 06½ | 71 13 | 79 55 | *n* |
| *N* 2$\bar{1}$0 | 105 49½ | 90 00 | 11 30 | 105 49½ | 80 02½ | — |
| *M* 1$\bar{1}$0 | 116 10 | 90 00 | 21 50½ | 116 10 | 80 47½ | *b* |
| *L* 2$\bar{3}$0 | 124 57½ | 90 00 | 30 38 | 124 57½ | 81 41½ | — |
| *K* 1$\bar{2}$0 | 132 12½ | 90 00 | 37 53 | 132 12½ | 82 34 | *e* |
| *J* 1$\bar{3}$0 | 142 54½ | 90 00 | 48 35 | 142 54½ | 84 04½ | — |
| *I* 1$\bar{4}$0 | 150 05½ | 90 00 | 55 46 | 150 05½ | 85 12 | — |
| *w* 011 | 23 26½ | 24 57½ | 82 03½ | 67 13½ | 22 18½ | — |
| *x* 021 | 12 21 | 40 53 | 84 45½ | 50 15½ | 39 16½ | — |
| *W* 0$\bar{1}$1 | 155 42½ | 24 14 | 78 40 | 111 58 | 22 26½ | *x* |
| *X* 0$\bar{2}$1 | 167 24½ | 40 20½ | 79 08½ | 129 11 | 39 39½ | — |
| *Y* 0$\bar{3}$1 | 171 33½ | 51 35½ | 80 02 | 140 49 | 51 17 | — |
| *d* 101 | 93 15 | 50 03½ | 39 57 | 99 29½ | 39 37 | — |
| *D* $\bar{1}$01 | −84 07½ | 39 34 | 129 33 | 86 16 | 49 59 | — |
| *p* 111 | 73 36 | 51 11 | 43 13 | 77 17½ | 41 02½ | — |
| *r* $\bar{1}$11 | −58 31½ | 43 56½ | 128 08 | 68 45½ | 52 54 | *m* |
| *t* $\bar{1}\bar{1}$1 | −112 07½ | 41 35 | 126 33½ | 104 28½ | 51 35 | — |
| *q* 121 | 57 10 | 54 50 | 49 21 | 63 41½ | 45 58 | — |
| *s* $\bar{1}$21 | −41 43½ | 51 00 | 124 01 | 54 32½ | 58 02½ | — |
| *u* $\bar{1}\bar{2}$1 | −132 29 | 48 06 | 120 37½ | 120 11 | 56 27½ | — |

Habit: Cuboidal, with prominent development of the axial zones; thick tabular {010} In crystal aggregates; granular.

Cleavage: {010} perfect; also {001}, less good.

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[1] Grailich (*Ber. Akad. Wien*, **28,** 272, 1858).

[2] Ungemach (*Bull. Soc. franç. Min.*, **58,** 162, 1935), on crystals from Chile, transformed to the normal setting. Ungemach retained the setting of Linck (*Zeits. Krist.*, **15,** 23, 1888) which was also accepted by Dana (*System*, 1892). Goldschmidt (*Winkeltabellen*, 1897; *Atlas*, **7,** 1922) took another position. The adopted axial directions agree with those of Blaas (*Ber. Akad. Wien*, **88** (1), 1121, 1884), as corrected by Goldschmidt (*Index*, **3,** 45, 1891), if allowance is made for his poor measurements.

*Transformations:* Blaas to normal position. 100/020/001; Linck to normal position 010/$0\bar{1}\bar{1}$/$\bar{1}00$; Goldschmidt to normal position: $0\bar{1}0$/$\bar{1}00$/$00\bar{1}$.

[3] Ungemach (1935), relettered; the following forms of Linck (1888) are rejected as erroneous: *m*{320}, *y*{508}, *t*{0.$\bar{5}$.18} (Linck's notation).

The author is indebted to Dr. M. A. Peacock for outlining this study and for assistance in preparing the manuscript.

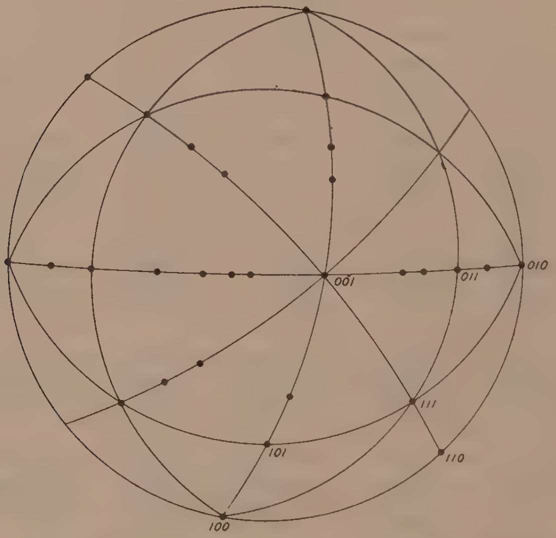

Fig. 1. Römerite: stereographic projection of the accepted forms, after Ungemach (1935). The position is that of Linck (1888), adopted by Dana (1892).

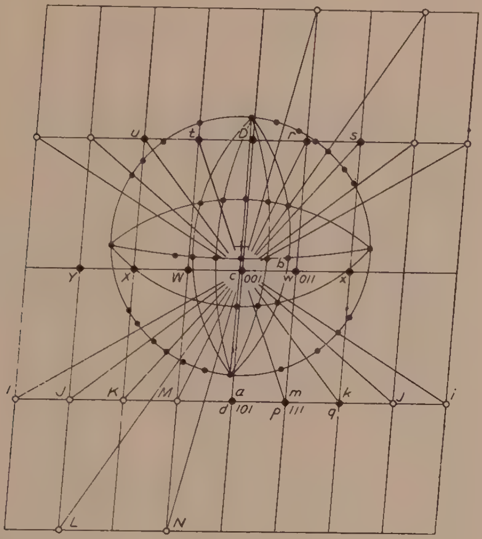

Fig. 2. Römerite: stereographic-gnomonic projection of the accepted forms in normal position.

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# HASTINGSITE IN THERALITE FROM THE CRAZY MOUNTAINS, MONTANA

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Among the many occurrences of theralite in the Crazy Mountains, amphibole occurs in notable amount only in the large laccolith, 100 feet thick, forming the crest and west slope of a large anticline in which a number of sills and laccoliths of alkaline rocks are interbedded with shales and sandstones of the Fort Union formation. The igneous rocks are folded with the sediments and were probably intruded at the time of the folding.

*Theralite.* The theralite (No. 183 '07 in the author's collection) is of medium coarse grain, dark colored with glittering plates of biotite, long black prisms of augite, and white feldspar and nepheline. Olivine is also abundant in the specimen, notably so in the field, especially near the base of the laccolith and at the apex of the fold where large rounded nodules, several inches in diameter and elongated masses forming bands in the rock, are prominent. These suggest either gravity settling or straining out from the fluid magma by pressure.

The order of crystallization, as shown by the thin sections, is first the accessories, then olivine, biotite, augite, amphibole, nepheline, and feldspar. The pyroxenes have cores of diopsidic augite, grading outward through aegirite-augite to aegirite. The peculiar orthoclase in the theralites has over one per cent of BaO and SrO, also soda and some lime with the dominating potash. The biotite and nepheline show traces of barium; spectroscopically, there appears to be a trace of this oxide in the amphibole.

Table 1 gives an analysis of the theralite, together with the composition computed from the mode, as determined by the integrator. After silica, magnesia is the largest constituent; this corresponds to the abundance of olivine, and perhaps the presence of amphibole. This rock and one other, a hornblende picrite, have the highest percentages of magnesia in the whole igneous assemblage. In the Quantitative Classification the theralite is *Do-sodic* and *Pilandose.*

*Hastingsite.* A sample of the amphibole was separated from the rock by Professor E. S. Larsen in the Harvard Mineralogical Laboratory. In spite of difficulties of separation, due to adhering aegirite, the sample was found by Professor Larsen, and by the author, to be 99 per cent pure. The result of an analysis of the amphibole is given in table 2.

TABLE 1. ANALYSIS, COMPUTED COMPOSITION AND MODE OF THERALITE

| | A | B | | C |
|---|---|---|---|---|
| $SiO_2$ | 45.72 | 44.49 | | |
| $TiO_2$ | 0.76 | 2.14 | | |
| $Al_2O_3$ | 11.82 | 12.22 | | |
| $Fe_2O_3$ | 4.31 | 5.08 | Orthoclase | 7.6 |
| $FeO$ | 5.28 | 6.57 | Nepheline | 15.0 |
| $MnO$ | 0.14 | — | Noselite | 1.2 |
| $MgO$ | 13.01 | 11.54 | Augite | 40.9 |
| $CaO$ | 10.38 | 9.82 | Aegirite | 1.7 |
| $Na_2O$ | 3.44 | 3.84 | Amphibole | 5.7 |
| $K_2O$ | 2.84 | 3.31 | Biotite | 12.7 |
| $H_2O+$ | 1.35 | 0.39 | Olivine | 10.3 |
| $CO_2$ | none | — | Magnetite | 4.2 |
| $P_2O_5$ | 0.60 | 0.14 | Apatite | 0.1 |
| S | 0.18 | — | | |
| $Cr_2O_3$ | 0.07 | — | | |
| $SrO$ | 0.04 | — | | |
| $BaO$ | 0.22 | 0.44 | | |
| Cl | — | 0.08 | | |
| | 100.16 | 100.06 | | 99.4 |

A. Theralite (183 '07), Crazy Mountains, Montana; analyst, F. A. Gonyer. Specific gravity, 2.95.

B. Computed composition corresponding to the mode. $H_2O$ represents water of constitution of the fresh minerals, but neglects the water due to some zeolitization of the nepheline and noselite.

C. Mode of the theralite (Leitz integrator), by weight. Due to difficulty in counting, the value for apatite is too low; 0.06 per cent $P_2O_5$ gives 1.4 per cent apatite.

TABLE 2. ANALYSIS AND CONSTITUTION OF HASTINGSITE

| | | Mol. | Atoms/24 oxygen | |
|---|---|---|---|---|
| $SiO_2$ | 48.51 | 808 | Si | 7.1 |
| $TiO_2$ | 1.32 | 16 | Ti | 0.1 |
| $Al_2O_3$ | 6.60 | 65 | Al | 1.2 |
| $Fe_2O_3$ | 4.09 | 26 | Fe''' | 0.5 |
| $FeO$ | 9.48 | 132 | Fe'' | 1.2 |
| $MnO$ | 0.19 | 3 | Mn | 0.0 |
| $MgO$ | 14.79 | 370 | Mg | 3.3 |
| $CaO$ | 5.60 | 100 | Ca | 0.9 |
| $Na_2O$ | 6.01 | 97 | Na | 1.7 |
| $K_2O$ | 2.20 | 23 | K | 0.4 |
| $H_2O+$ | 1.47 | 82 | H | 1.4 |
| | 100.26 | | | |

Hastingsite, from theralite, Crazy Mts., Montana; analyst, F. A. Gonyer. Specific gravity, 3.23.

The amphibole has the constitution:

$$(Na, K)_2Ca(Mg, Fe'', Fe''', Al, Ti)_5(Al, Si)_8(OH)_2O_{22}$$

in which $Mg/Fe''=2.8$, $Al/Fe'''=2.5$, $Na/K=4.2$.

The amphibole occurs as an aggregate of grains, mainly subhedral, associated with imperfect prisms of aegirite from which the hastingsite is distinguished by the perfect amphibole cleavage and the characteristic pleochroism. Occasionally it is found in longer prisms with well-developed prismatic and terminal planes. On these crystals the optical properties on (010) and (100) were determined with the universal stage and strong monochromatic light from an arc and monochromator. The refractive indices were determined by immersion. In one case a prism of augite was found with parallel growths of aegirite-augite and hastingsite; $Z{:}c$ was 39° for augite, 68° for aegirite-augite, 38° for hastingsite, which was on the outside and the latest to crystallize. The hastingsite gave the following data:

| | | $n$(Na) | |
|---|---|---|---|
| $X$ (dull yellow) | $:c\ [001]=52°$ | 1.639 | Negative |
| $Y$ (liver brown) | $=b\ [010]$ | 1.658 | $2V$ (Na)$=38°$[1] |
| $Z$ (greenish brown) | $:c\ [001]=38°$ | 1.660 | $r<v$, strong |

This hastingsite differs from the examples given by Larsen and Berman (1934) in several ways: the refractive indices are lower than those of any of the examples listed; the double refraction (0.021) is higher than that of any except the ferrohastingsite (p. 191); the extinction angle and optic axial angle are unlike any in the list; the dispersion differs from that of all but one; and the pleochroism differs in tints, especially in the liver-brown color of $Y$. The specific gravity (3.23) lies within the range of those listed, the nearest being No. 57 (p. 227) with $G=3.26$.

Evidently the amphibole formed last of the mafic minerals and was succeeded by the nepheline and feldspar, the temperature of the magma decreasing, with concentration of the alkalis, causing a reaction with the diopsidic augite, changing it toward the periphery to aegirite-augite, and lastly to hastingsite.

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[1] 40° in the white arc.

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